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LOW-TEMPERATURE MODIFICATIONS OF AMMONIUM NITRATE, AND ITS COOLING AND QUENCHING

S. I. Volfkovich, S. M. Rubinchik, and V. M. Kozhin

In addition to the four crystalline modifications of ammonium nitrate that exist at normal pressure and at temperatures above 0° (I, cubic, 169-125°; II, tetragonal, 125-84.5°; III, β -rhombic, 84.5-32.4°; IV, α -rhombic, 32.4° to -16°), there are known also one modification that exists below 0° (V, tetragonal, stable below -16°) and one modification that exists at pressures higher than 9000 kg/sq. cm and temperatures above 169.2°.

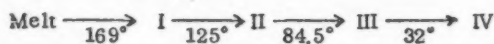
There are indications in the literature that a transformation of ammonium nitrate occurs also in the region -50° to -65°. Hendricks and coworkers [1], who detected a small anomalous change in the specific volume at -50°, point out that the X-ray diagrams for ammonium nitrate powder at -33° and -78° are very similar. Crenshaw and Ritter [2], who studied the variation of the specific heat of NH_4NO_3 with temperature, obtained a maximum on the specific heat - temperature curve at -60.4°. In an analysis of these results, Meerman [3] pointed out quite rightly that the curve should have had a maximum at -16°, since there can be no doubt in the existence of a transition at -16° ($\text{IV} \rightleftharpoons \text{V}$); but the authors concerned detected no maximum at -16°. Meerman considers that there is no transition at -60.4°, but only retardation of the establishment of equilibrium, which is observed for a number of ammonium salts at low temperatures. Jaffray [4], using the differential-thermal method, found the transition temperature of NH_4NO_3 to be -57° to -60°. He noted also a transition in the region -150° to -160°, but mentioned this only in passing. Volkringer and coworkers [5] have noted an anomaly in the Raman spectra of ammonium nitrate between -75° and -192°.

In view of the meager study that has been devoted to the behavior of ammonium nitrate at low temperatures, we have investigated the transformations of this salt with the aid of differential thermal analysis, microcinematography, and X-ray analysis. Microcinematography of the polymorphic changes of ammonium nitrate was first carried out in the range 170-20° in 1940 by one of the authors of the present paper, working with Glazova [6] in the Laboratory of Scientific and Applied Photography and Cinematography of the Academy of Sciences of the USSR.

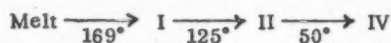
EXPERIMENTAL

In the present investigation we have studied the behavior of the salt when cooled to -196°. We have made use of Tsurinov and Volnova's universal cooling and heating stage in this work, the cooling agent employed being liquid nitrogen. The temperature was determined by means of a fine thermocouple (platinum and platinum-rhodium; $d = 0.1$ mm).

A 0.001-0.002 g sample of dry ammonium nitrate was placed on a slide, covered with a cover glass, and carefully heated to melting. The fused ammonium nitrate was slowly cooled (1-1.5° per minute) under the microscope in polarized light (magnification 8 x 10), and the four transitions to crystalline modifications were clearly perceived (Figures 1-4).



When the rate of cooling exceeded 2° per minute, only three transitions were observed:



i.e., when cooling is at more than 2° per minute the modification III is not detected, and instead of the points

84.5° and 32°, the point 50° is found. This transition was recorded on cinecolor film, a very clear picture being obtained.

The large polyhedra of II were converted into a needlelike polycrystal (Fig. 5). No visible changes occurred in the polycrystal when it was preserved in a desiccator for 14 days.

In order to clarify the meaning of the pictures obtained by microcinematography, we took cooling curves. On these curves (Figures 6-9), which were plotted for various cooling rates (1.5-30° per minute) and for samples of 0.02-0.15 g, the same breaks were always obtained; they corresponded to the transitions:

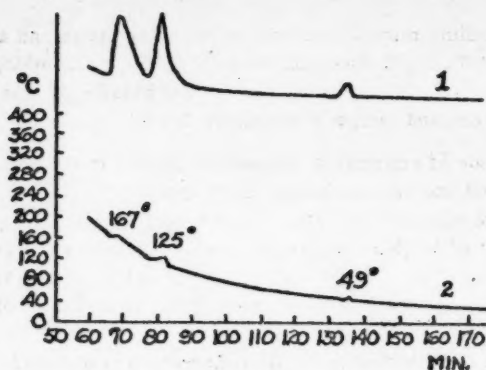
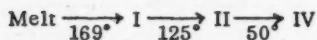


Fig. 7. Cooling curve for NH_4NO_3 : R_D 2000 ohms; R_d 150 ohms; cooling rate 1.9°/min; wt. 0.15 g. 1) Differential plot; 2) direct plot.



We were unable to plot the cooling curve for a very small sample of fused ammonium nitrate

(0.001-0.002 g, as we took for the microscopic investigation), in which all four transitions should have been found. We carried out trials in which the sample was heated at above 125°, but below the melting point, and was then cooled; the transition $\text{II} \xrightarrow{50^\circ} \text{IV}$ was again found (Figures 10 and 11). But we obtained a quite clear indication of the transition $\text{III} \xrightarrow{84.5^\circ} \text{IV}$ on the cooling curves of ammonium nitrate

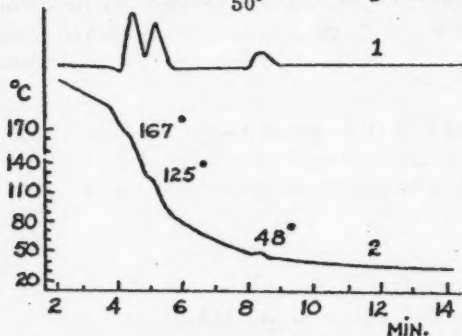


Fig. 9. Cooling curve for NH_4NO_3 : R 1000 ohms; R_d 100 ohms; cooling rate 30°/min; wt. 0.05 g. 1) differential plot; 2) direct plot.

* R_D = Resistance direct; R_d = Resistance differential.

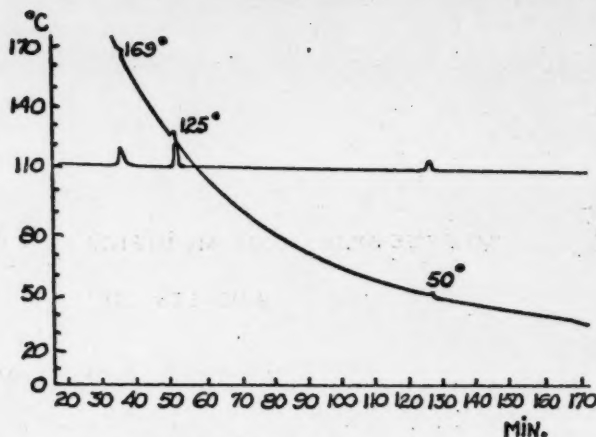


Fig. 6. Cooling curve for NH_4NO_3 : R_D 900 ohms; R_d 740 ohms; cooling rate 1.5°/min; wt. 0.02 g.

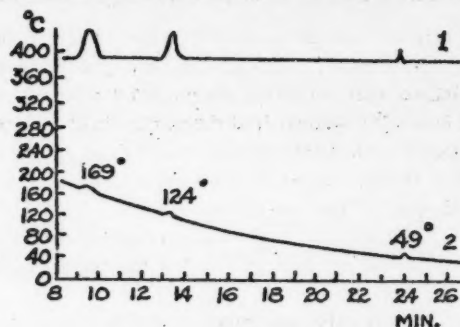


Fig. 8. Cooling curve for NH_4NO_3 : R_D 2000 ohms; R_d 150 ohms; cooling rate 8.3°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

preheated at below 125° with samples of the order of 0.02-0.15 g (Figures 12 and 13).

The transition at 50° was studied microscopically by Bowen [7], who stated that the transition occurs very readily, both when cooling, and also when heating. According to Hendricks and coworkers [1], the transformation can be repeated many times by heating and cooling, so long as the sample is dry and in the form of a thin film. In a thick layer Modification III is formed after 3-4 transitions. Tiemeyer [8] confirmed this transition by X-ray analysis. He pointed out that it is impossible to repeat the transition $\text{II} \rightleftharpoons \text{IV}$ a large number of times by repeated alteration of the temperature, since



Fig. 1. Modification I, cubic. The darkening on the right is incipient I \rightarrow II transition.



Fig. 2. Modification II.



Fig. 3. Modification III.



Fig. 4. Modification IV.



Fig. 5. Polycrystal of NH_4NO_3 after II \rightarrow IV transition.



Fig. 22. X-Ray diagrams of NH_4NO_3 : a) Modification IV; b) Modification V; c) Modification VII.



Fig. 23. X-Ray diagram of NH_4NO_3 quenched at -196° .

Fig. 24. X-Ray diagram of NH_4NO_3 quenched at -20° .

Note: Figs. 18, 19, and 20 in the original are color photographs, which can not be reproduced in color by the process used for publication of this translation. The predominant colors in each photograph are therefore indicated on the black-and-white reproductions below. Publisher.

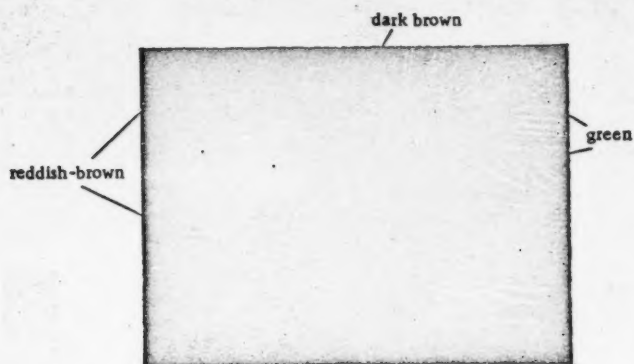


Fig. 18. Modification V.



Fig. 19. NH_4NO_3 at -100° .



Fig. 20. NH_4NO_3 below -170°
(Modification VII has formed).

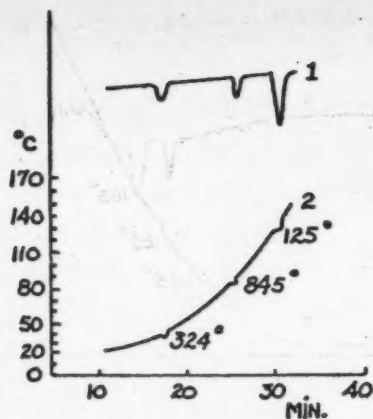


Fig. 10. Heating curve for NH_4NO_3 ; R_D 1000 ohms; R_d 100 ohms; heating rate 7°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

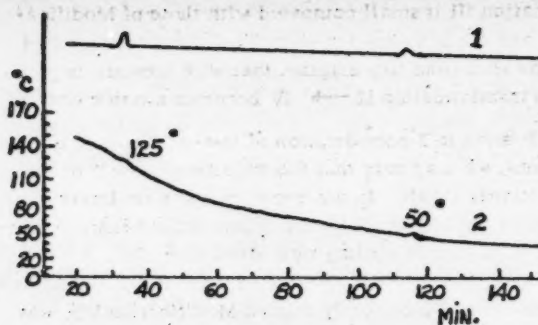


Fig. 11. Cooling curve for NH_4NO_3 ; R_D 1000 ohms; R_d 100 ohms; cooling rate 1°/min; wt. 0.03 g. 1) Differential plot; 2) direct plot.

polycrystalline transformation occurs with formation of Modification III. One of us, working with Glazova [6] has observed a transition of NH_4NO_3 , both during cooling and during heating, in the region 47-55° (in addition to the transitions at 125°, 84.5°, 32.4°, and -16°).

Nikonova [9] determined the $\text{II} \rightarrow \text{IV}$ transition point thermographically, the cooling curves being plotted by the aid of a Kurnakov pyrometer. On heating curves, she did not observe this transition. Some investigators, e.g. Early and Lowry [10], consider that we are concerned here not with a transition, but with supercooling of Modification III.

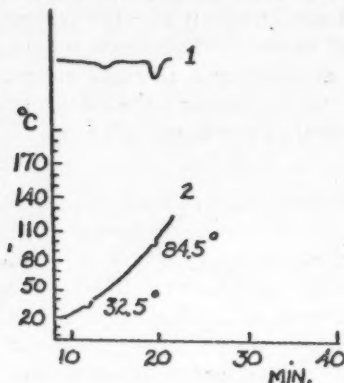


Fig. 12. Heating curve for NH_4NO_3 ; R_D 1000 ohms; R_d 100 ohms; heating rate 8.8°/min; wt. 0.02 g. 1) Differential plot; 2) direct plot.

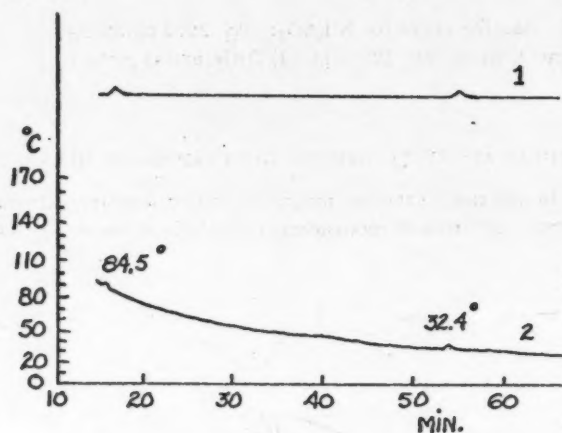
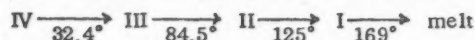


Fig. 13. Cooling curve for NH_4NO_3 ; R_D 1000 ohms; R_d 100 ohms; cooling rate 1.4°/min; wt. 0.02 g. 1) Differential plot; 2) direct plot.

We must point out that on our heating curves (Figures 14-16), which were plotted for various rates of heating (7.3-60°/min.), four distinct breaks are always found, corresponding to the following four transformations:



We, like Nikonova, never observed the transition $\text{IV} \rightarrow \text{II}$ on heating curves, even when samples that had just (10-20 minutes before) undergone the transformation $\text{II} \xrightarrow{50^\circ} \text{IV}$ were heated.

It will be seen from the pressure-temperature diagram of the fields of existence of modifications of ammonium nitrate constructed by Bridgman [11] (Fig. 17) from his own results and those of other investigators

(Modification VII has been inserted by us) that the field of Modification III is small compared with those of Modifications II and IV; it tapers out when the pressure is increased. It will be seen from this diagram that with increase in pressure the transformation II \rightarrow IV becomes a stable one.

Passing to a consideration of low-temperature transformations, we may note that the transition IV \rightarrow V occurs comparatively slowly. In our experiments, after formation of Modification V (Fig. 18), ammonium nitrate remained unchanged with further cooling right down to -170° . At -170° a polymorphic transformation occurred, and a new modification, which may be correctly termed Modification VII, was formed.

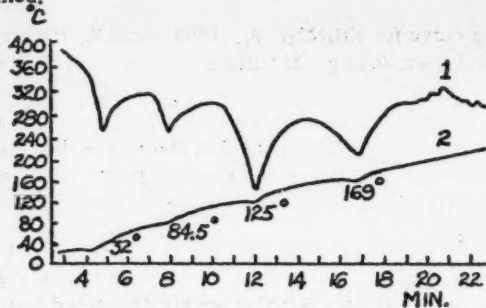


Fig. 15. Heating curve for NH_4NO_3 : R_D 2000 ohms; R_d 150 ohms; heating rate $12^\circ/\text{min}$. 1) Differential plot; 2) direct plot.

the transition at -170° corresponds to an exothermic effect.

In addition to the thermographic and microcinematographic investigations, we made an X-ray investigation with copper radiation at room temperature and at low temperatures. ** We used Kozhin's universal apparatus [12],

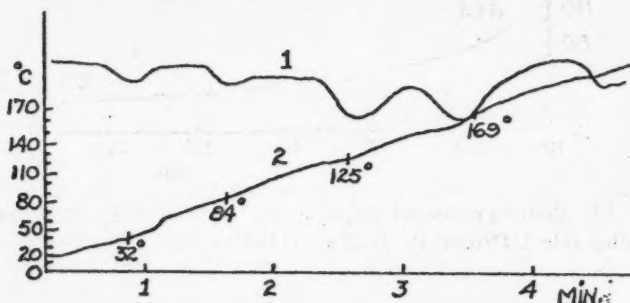


Fig. 16. Heating curve for NH_4NO_3 : R_D 1000 ohms; R_d 100 ohms; heating rate $60^\circ/\text{min}$; wt. 0.03 g. 1) Differential plot; 2) direct plot.

alcohol and solid carbon dioxide) after five minutes' treatment (the temperature of the sample was measured with a copper-constantan thermocouple).

* The color photomicrographs are reproduced in black and white (see plate, page 170).

** The investigation was carried out in the X-ray Structure Laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

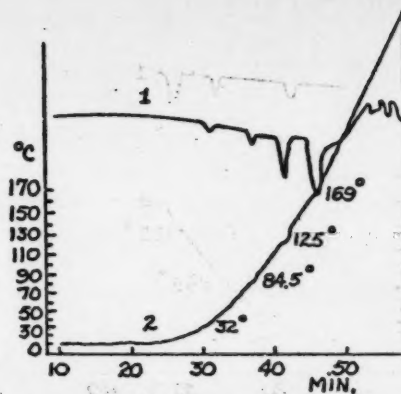


Fig. 14. Heating curve for NH_4NO_3 : R_D 1000 ohms; R_d 100 ohms; heating rate 7.3° per minute; wt. 0.03 g. 1) Differential plot; 2) direct plot.

At the polymorphic transition point the optical properties of the polycrystal were altered, and the interference colors observed by transmitted polarized light were changed. In Figures 19 and 20 we give color photomicrographs of the polycrystal of ammonium nitrate at -100° (before the transition) and below -170° (after the transition). * The peculiar decolorization of the polycrystal will be seen. On the cooling curve (Fig. 21), plotted for a cooling rate of 6.3° per minute,

The sample of ammonium nitrate, diameter 1 mm and height 5 mm, was set up on a goniometric head and covered with a cellophane thimble, diameter 8 mm and height 10 mm, which is necessary for the mechanical protection of the sample from the fine stream of cooling agent (liquid nitrogen or a mixture of alcohol and solid carbon dioxide). The sample attained the temperature of the coolant (-196° for liquid nitrogen, -20° for a mixture of

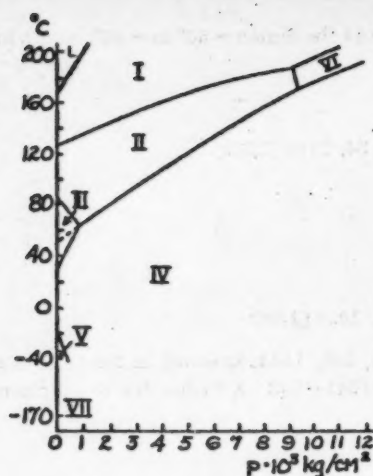


Fig. 17. Fields of existence of NH_4NO_3 modifications.

In the X-ray study of quenched samples, the ammonium nitrate was melted in a thin-walled capillary and rapidly cooled to the required temperature. This temperature was maintained during the whole of the exposure. The presence of the glass capillary gave additional background to the X-ray picture, and this made it difficult to detect weak lines. The X-ray pictures for ammonium nitrate at $+20^\circ$, -20° , and -196° (Fig. 22) differ appreciably from one another. This confirms the microcinematographic and thermographic results relating to the existence at below -170° of a low-temperature modification, differing in its structure from Modifications IV and V.

Apart from the low-temperature modifications, we have investigated samples of quenched (rapidly cooled) ammonium nitrate by means of microcinematography; such work is of interest in connection with the better physico-mechanical properties of a salt obtained in this way. Volfkovich and Glazova [6] have shown that the quenched product is of lower hygroscopicity and has less tendency to cake. Their results indicating that more than one phase is formed are not contradicted by the present investigation. The X-ray pictures of ammonium nitrate quenched at -196° (Fig. 23), and not quenched, but photographed at -196° (Fig. 22c) are somewhat similar with respect to the distribution of the lines.

The X-ray diagrams of samples quenched at -196° (Fig. 23) and not quenched but photographed at $+20^\circ$ (Fig. 22a) are also similar with respect to the distribution of interference lines. It is probable that quenching to -196° results in the formation of Modification IV and Modification VII. The X-ray diagram of ammonium nitrate quenched at -20° (Fig. 24) shows that the sample consists of crystallites (grains) of the order of not less than 10^{-2} – 10^{-3} cm. The structures of Modification V (Fig. 22b) and of the sample quenched at -20° (Fig. 24) differ in that the crystallites of the latter are larger.

Our measurements of the extrusion pressure of ammonium nitrate quenched at -20° showed that this is lower than that of Modification V by a factor of about 3.5. Ammonium nitrate quenched at -20° probably contains Modification V and possibly also IV, but not III, since we have already shown that at cooling rates of greater than 1.5° per minute Modification III cannot be detected on the cooling curves even for samples of 0.02–0.03 g.

SUMMARY

1. The existence of a low-temperature modification of ammonium nitrate at below -170° has been confirmed by microcinematographic, X-ray structure, and thermographic analysis; it may be suitably named Crystalline Modification VII.

2. When fused ammonium nitrate is cooled at a rate of more than 2° per minute, metastable transformation of Modification II to Modification IV occurs, but the reverse change is not observed when the temperature is raised.

3. Ammonium nitrate quenched at -20° consists mainly of Modifications V and IV. As can be seen from cooling curves plotted for different cooling rates, Modification III will be absent. Ammonium nitrate quenched at

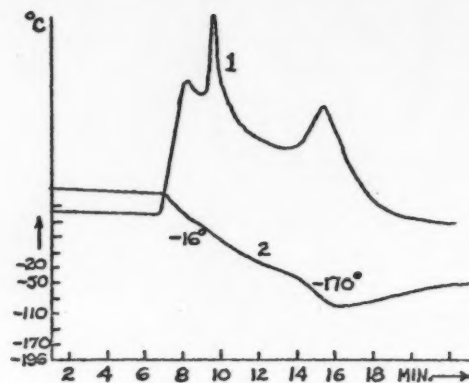


Fig. 21. Cooling curve for NH_4NO_3 : R_D 2300 ohms; R_d 1200 ohms; cooling rate $6.3^\circ/\text{min}$. 1) Differential plot; 2) direct plot.

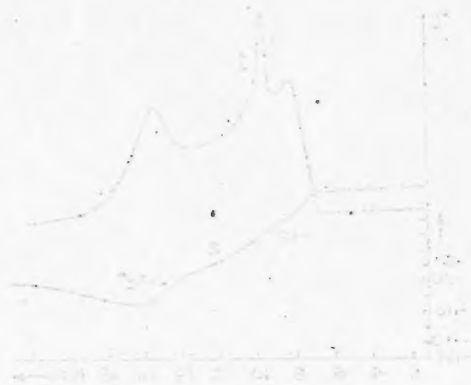
- 196° consists of Modifications IV and VII.

4. We have not detected the transformation of ammonium nitrate in the region - 50° to - 65°, which has been found by some workers.

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SORPTION OF WATER VAPOR BY ACTIVE CHARCOALS

M. M. Dubinin and E. D. Zaverina

Isotherms for the sorption of water vapor by active charcoals differ greatly in form from those for the sorption of organic vapors. For relative equilibrium pressures in the region of 0.4, water vapor is not adsorbed strongly by active charcoal. The isotherm has a concave form, and for ashless charcoals, e.g., that prepared from sucrose, the sorption and desorption curves coincide in this region. At higher relative pressures, there are sharp rises in the sorption and desorption curves, with formation of the hysteresis loop characteristic of water vapor when the pores of the charcoal are not too small [1].

The initial, reversible part of the isotherm, up to the point where hysteresis begins, represents the process of adsorption of water vapor; the irreversible, steeply rising part of the curve is generally associated with capillary condensation of vapor. Our previous detailed investigation of the isotherms for the sorption and desorption of water vapor at the surface of ashless sucrose charcoals activated in varying degree led to the formulation of a working hypothesis, according to which the sorption of water vapor by active charcoals is the sum of two processes: adsorption and capillary condensation [1]. It was supposed that the main condition for the occurrence of capillary condensation in the pores of the charcoal was the formation of a condensed monomolecular adsorbed layer as a result of a phase transition of the two-dimensional vapor at a definite equilibrium pressure for surface sites of constant heat of adsorption. This condition may be observed at relative vapor pressures higher than those calculated from the pore dimensions by Thomson's equation. The process of capillary condensation then takes on a forced character.

Juhola and Wilg conclude from the results of their experiments that in the hysteresis region the sorption and desorption curves of the isotherm correspond to capillary condensation and evaporation of water for different wetting angles, namely, $\cos \theta = 0.49$ for desorption and $\cos \theta = 0.28$ for sorption [2,3]. With such an assumption it becomes possible, from the theory of capillary condensation and the sorption and desorption isotherms for water vapor, to calculate structure curves for active charcoals and differential curves for the distribution of pore volume according to pore radius.

We should, of course, be provided with a sounder basis for the hypothesis of the capillary condensation of water vapor if the sorption isotherms for water vapor on nonporous carbon adsorbents were found to differ essentially in their character in their central parts from those for water vapor on active charcoal. The sharp rise in the isotherms for active charcoals in the 0.4-0.6 range of relative pressures might then be directly associated with the presence of a porous structure and with a capillary-condensation process. In the present investigation we have undertaken the task of making a comparative study of sorption and desorption isotherms for water vapor on nonporous and porous carbon adsorbents having surfaces that cannot differ at all appreciably in chemical nature.

EXPERIMENTAL

As our nonporous carbon adsorbent, we took thermally treated carbon black having spherical particles. The carbon black was heated in a vacuum at 950°. In the experiments the carbon black was used both in the powder form and as briquets prepared without the aid of binding materials.

The sorption and desorption isotherms for benzene and water vapors were determined by the sorption-balance vacuum method [4]. The preliminary evacuation of the adsorbents was effected by means of a three-stage mercury vapor pump; it was continued for six hours at 450°. In the sorption and desorption experiments, particular attention was paid to the attainment of an equilibrium state.

Sorption and desorption isotherms for benzene vapor on thermally treated carbon black powder at 20° are shown in Fig. 1. For relative pressures of up to 0.78, the adsorption and desorption points are closely represented by a single curve. At higher relative pressures, there is a sharp rise in the sorption curve, mainly due to capillary condensation of benzene vapor in the spaces formed between the carbon black particles. The desorption isotherm is now not coincident with the sorption isotherm, and the two curves form the hysteresis loop that is characteristic of capillary condensation. The limit of sorption is at 11.6 mmole/g.

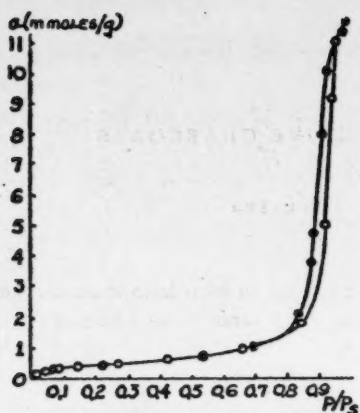


Fig. 1. Sorption and desorption isotherms for benzene vapor on carbon black at 20°.

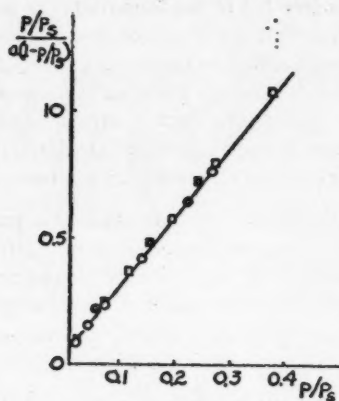


Fig. 2. Adsorption and desorption isotherms for benzene vapor at 20° in linear form. Adsorption: ○ - carbon black powder; □ - carbon black briquet. Desorption: ● - carbon black powder; ■ - carbon black briquet.

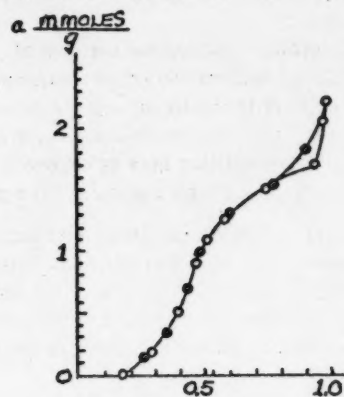


Fig. 3. Sorption and desorption isotherms for water vapor on carbon black at 20°: ○ - adsorption; ● - desorption.

In Fig. 2, the experimental results for the adsorption of benzene vapor at 20° for powder-form and briquet carbon blacks are represented in linear form in accordance with the adsorption-isotherm equation of Brunauer, Emmett, and Teller [5]. The value of the adsorption of benzene vapor calculated for a compact monolayer on carbon black from the constants of the equation is $a_m = 0.365$ mmole/g. If we assume, in accord with the results of Kiselev, Karnaukhov, and Khrapova [6], that the most probable value of the molecular area of benzene in a monolayer for a similar sample of carbon black is 46.5 \AA^2 (not differing greatly from the value of 41 \AA^2 , found by Smith and Pearce [7]), then the specific surface of the investigated sample of carbon black will be 103 sq.m/g . A statistical treatment of numerous electron-microscope photographs, which was carried out in our laboratory by Radushkevich and Lukyanovich, has led to a value of 98 sq.m/g for the specific surface of the carbon black. The close agreement of the results of adsorption and electron-microscope measurements shows that the sample of carbon black was indeed a nonporous carbon adsorbent.

Fig. 3 represents sorption and desorption isotherms for water vapor on carbon black at 20°, as determined by the vacuum sorption-balance method. In the range of low relative pressures, the adsorption of water vapor is immeasurably small; in the middle range of relative pressures adsorption is reversible, and there is a steep rise in the isotherm. The inflexion point on the curve at a relative pressure of 0.55 corresponds to an adsorption of $a = 1.20$ mmole/g. As limiting sorption is approached, there is again a sharp rise in the isotherm, and in this range of relative pressures the sorption and desorption isotherms do not coincide, a characteristic hysteresis loop being formed.

According to Harkins and Jura the molecular area in a compact water monolayer is 14.8 \AA^2 [8]. For a specific surface in the carbon black of 103 sq.m/g , completion of a monolayer corresponds to an adsorption of $a_m = 1.15 \text{ mmole/g}$. This value corresponds almost exactly to the completion of the main rise of the isotherm and its point of inflection at $a = 1.20 \text{ mmole/g}$. Hence, for carbon black, and for relative pressure of up to 0.55, adsorption is on the average monomolecular. Polymolecular adsorption at higher pressures is complicated by the closeness to saturation for capillary condensation of water vapor in the spaces formed by spherical carbon black particles arrayed in contact with one another.

As our porous carbon adsorbents, we took four samples of active wood charcoal, prepared with the assistance of Chepurnoi [9]. The conditions of its thermal treatment at 950° were exactly the same as those used for carbon black. In general character, the sorption isotherms for water vapor did not differ from those obtained on carbon black. The main rise of the isotherm was in the 0.4-0.6 range of relative pressures, both for active charcoals and for carbon black.

By way of example, sorption isotherms for water vapor on carbon black and on charcoal No. 1 are shown, with different scales along the ordinate axis, in Fig. 4. The regions of sharp rise are somewhat displaced from one

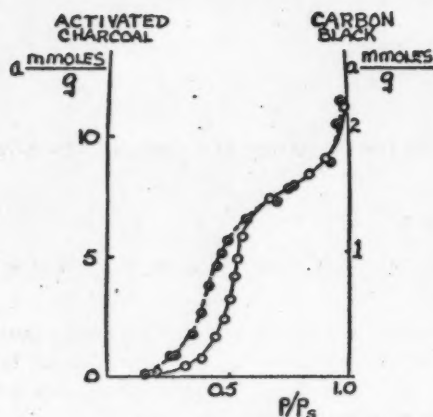


Fig. 4. Sorption isotherms for water at 20° on carbon black (●) and activated charcoal (○).

another, which is to be explained by a small difference in the properties of the surfaces of active charcoal and carbon black. The points of inflexion on both isotherms at a relative pressure of about 0.55 evidently correspond to completion of the formation of a compact monomolecular adsorbed layer. After this, the surface properties of the carbon black and active charcoal become almost identical, and the adsorption isotherms coincide over the 0.55-0.95 range of relative pressures, in which polymolecular adsorption occurs.

The coincidence of these adjusted isotherms in the range of relative pressures indicated is evidence of the mathematical affinity of the curves.

The mathematical condition for the affinity of the isotherms may be written:

$$a_1 = f(p/p_s); \quad (1)$$

$$a_2 = k f(p/p_s), \quad (2)$$

where a_1 is the adsorption on carbon black; a_2 is the adsorption on active charcoal; k is the affinity coefficient.

Expressing the isotherm equations in the form of inverse functions, we have:

$$p/p_s = \varphi(a_1) \quad (3)$$

$$p/p_s = \varphi(a_2/k) \quad (4)$$

and for the adsorption values a_1 and a_2 corresponding to identical relative pressures in the range under consideration, taking into account that the function φ is not periodic, we obtain:

$$a_2 = k a_1, \quad (5)$$

i.e., a linear relation between a_2 and a_1 .

The graphs in Fig. 5 will serve as proof of the affinity of the adsorption isotherms for water vapor on carbon black and on the studied samples of active charcoal in the 0.55-0.95 range of relative pressures; the points corresponding to the adsorption values for each of the active charcoals and the carbon black at identical relative pressures. These points, obtained by interpolation on the water vapor sorption isotherms for each sample of charcoal, fit closely to straight lines passing through the origin. With the chosen disposition of the axes of coordinates, the reciprocals of the slopes of the lines are affinity coefficients for the isotherms.

In Table 1 we give the affinity coefficients of the isotherms for the region of polymolecular adsorption, as determined from the graphs in Fig. 5. Since dispersion forces do not play a determining part in this region of water vapor sorption, the porous structure of the adsorbent cannot have a significant effect on the adsorption [10]. Hence, the affinity of the isotherms in the 0.55-0.95 range of relative pressures is evidence for the coincidence of the absolute adsorption isotherms, in the construction of which adsorption values are expressed in terms of unit area of adsorbent. Thus, in the case under consideration, the affinity coefficient is equal to the ratio of the

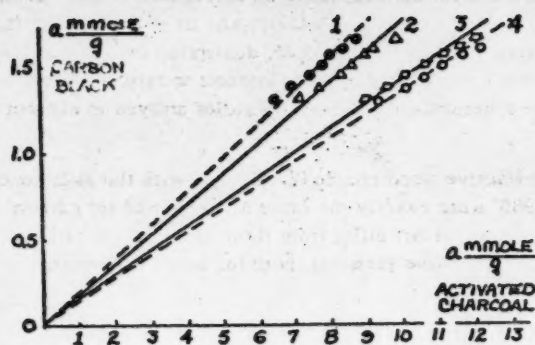


Fig. 5. Relation between values of the sorption of water vapor at 20° on carbon black and on active charcoals (nos. 1-4) for identical equilibrium pressures.

TABLE 1
Affinity Coefficients of Isotherms and Specific Surfaces of Active Charcoals

Adsorbent	Affinity coefficient of isotherm, k	Specific surface, s (sq.m/g)
Carbon black	1.00	103
Charcoal 1	5.15	530
" 2	5.75	590
" 3	7.08	730
" 4	7.42	765

specific surface of the active charcoal to that of the carbon black. The specific surface of a charcoal may therefore be expressed by the formula:

$$s = 103 \cdot k \text{ sq.m/g,}$$

(103 sq.m/g is the specific surface of the carbon black). The specific surfaces of the investigated samples of active charcoal, calculated in this way, are given in Table 1.

According to the concepts that we have developed in our laboratories, the steep rise in the adsorption isotherm for water vapor on carbon adsorbents is associated with the formation of a condensed monomolecular adsorbed layer, a major role in this process being the formation of hydrogen bonds [11-13]. In a consideration of the possible mechanism for the sorption of water vapor, it is necessary to take the nature of the adsorbent surface into account.

In our experiments, after thermal treatment at 950° the active charcoals and carbon black were brought into contact with air. Hence, as a result of activated adsorption (chemisorption), surface oxides were formed, and these could not be destroyed in the preliminary evacuation of the carbons at 450°. It may be supposed that, in the region of low equilibrium pressures, adsorption of water vapor is associated mainly with the formation of hydrogen bonds between adsorbed water molecules and surface oxides on the carbon adsorbents [13]. As a result of the relatively low energy of the hydrogen bond, adsorption is low.

Adsorbed water molecules form a special type of secondary adsorption centers, which may hold other molecules by hydrogen bonds. As a result of this, patches of a two-dimensional condensed phase appear as the pressure rises, these being formed of water molecules held by hydrogen bonds. The probability of the occurrence of this process will rise as the pressure increases up to a certain point, owing to increase in the number of adsorption centers. At a sufficiently high pressure the patches will merge, and a continuous condensed monomolecular layer will be formed. The steep rise in the isotherm in the middle range of relative pressures is probably to be associated with this peculiar process of the formation of two-dimensional patches of liquid, which proceeds until they merge together.

In considering the question of the stability of the associated complexes of water molecules in the form of patches of a condensed two-dimensional phase, which are formed on the surface of carbon adsorbents, two factors must be taken into account: the first is concerned with the surface oxides, which act as primary adsorption centers, and the second is concerned with the adsorption field, which is relatively weak in our case, and is due mainly to dispersion forces. Although water molecules are not associated in the gas phase since the thermal energy of movement is sufficient to break down complexes that form, the complexes are stabilized in the surface field of the adsorbent, and they become stable [12].

The increased adsorption potentials of dispersion forces in the fine pores of active charcoal increase still more the stability of these complexes of associated water molecules and make their formation possible at somewhat lower relative pressures in the gas phase. It is possible that it is this effect that causes the shift of the steep part of the sorption isotherm for water vapor toward lower pressures in a series of charcoals of various degrees of activation when we pass from relatively coarsely porous to more finely porous charcoals [1].

The nature of this shift requires more detailed study. In particular, it is important to evaluate the possible differences in the surface chemical properties of charcoals of various degrees of activation, i.e., having widely different carbonization treatments.

When the condensed monomolecular adsorbed layer has been formed, further rise in relative pressure results in the polymolecular adsorption of water vapor, which is complicated by capillary condensation when the porous structure of the active charcoal favors this process. In the case of the active charcoals that we have studied, capillary condensation comes into consideration when the main rise of the sorption isotherm, corresponding to the formation of a condensed monolayer, is complete. We may judge whether polymolecular adsorption or capillary condensation plays the determining role in the sorption of water vapor at relative pressures of greater than 0.55 by a consideration of the limiting sorption values expressed in relation to 1 sq.m of the charcoal surface. In the case of capillary condensation, the main factor determining the limiting sorption at a relative pressure of unity, will be the volume of fillable pores. It is difficult to imagine that this quantity will be directly proportional to the adsorbent surface. On the other hand, if polymolecular adsorption is of determining significance, the absolute values of the limiting sorption will lie close together for different charcoals. The results of the relevant calculations from the experimental data are given in Table 2.

TABLE 2

Limiting Sorption Values per Unit Surface of Active Charcoals

Adsorbent	Specific surface, s (sq.m/g)	Limiting sorption	
		a_s (mmole/g)	$\alpha_s = a_s / s$ (mmole/sq.m)
Carbon black	103	2.21	0.021
Charcoal 1	530	11.3	0.021
" 2	590	12.6	0.021
" 3	730	14.9	0.020
" 4	765	15.8	0.021

The almost identical limiting values for the sorption of water vapor (α_s) for nonporous carbon black and the samples of active charcoal examined indicate that, in the direct sorption process, the region of polymolecular adsorption extends right up to high relative pressures, approaching unity in value. In our cases of sorption, capillary condensation may play only a very small part. However, if as a result of polymolecular adsorption and, to some extent, capillary condensation with attainment of the sorption

limit, even a part of the finer pores of the active charcoal is filled, then the possibility cannot be excluded that in the desorption process the emptying of the pores will occur over a certain range of relative pressures, in accord with the theory of capillary condensation. A more detailed study of this aspect of the sorption process will be made in our further investigations.

The basic idea, therefore, of our previously developed concepts concerning the sorption of water vapor; namely, the formation of a condensed adsorbed film as a necessary condition for the occurrence of the process of capillary condensation, remains unchanged [1]. The described process, in which two-dimensional patches of water molecules associated together by means of hydrogen bonds are formed on the surface of carbon adsorbents and then merge into one another, is a two-dimensional phase transition, and is in many ways analogous to surface condensation; i.e., to a phase change of the first kind.

In the light of the results of the present investigation, the range of relative pressures in which the capillary condensation of water vapor is possible (in pores of active charcoal in the direct sorption process) must be moved to the higher range of relative pressures. The main rise in the sorption isotherm is not associated with capillary condensation, but with the formation of a condensed monomolecular adsorbed layer; i.e., with the stage preceding capillary condensation.

It should be noted that in certain cases, when the active charcoal has a suitable porous structure, the completion of the formation of a condensed adsorbed layer is not expressed by an appreciable inflexion in the sorption isotherm, owing to the superposition of the capillary condensation process.

SUMMARY

1. A detailed study has been made of the sorption isotherms for water vapor on nonporous, thermally-treated carbon black having a known specific surface, and also on a number of samples of active charcoal.

2. It has been shown that, for carbon black and active charcoals, the main rise in the sorption isotherm up to its point of inflexion corresponds to monomolecular adsorption. In the direct sorption process, the region of polymolecular adsorption extends up to high relative pressures, approaching 0.95. For the investigated samples

of active charcoal, the process of capillary condensation does not play an important part.

3. An exposition is given of the concepts developed in our laboratory concerning the mechanism of the sorption of water vapor by carbon adsorbents; it involves the hypothesis of the determining role of hydrogen bonds in the adsorption of water vapor. It is shown that the experimental results are in accord with these concepts.

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* See Consultants Bureau Translation, page 851.

NEW METHOD FOR THE INVESTIGATION OF THE MECHANISM

OF CATHODE PROCESSES, AND ITS APPLICATION

M. Smyalovsky and Z. Shklyarskaya-Smyalovskaya

The methods known at present for the investigation of the mechanism and kinetics of electronic processes do not permit us to give an unequivocal explanation of the nature of certain important phenomena accompanying the discharge of ions and separation of gases during electrolysis. This is particularly true of the problem of hydrogen overvoltage, which has long formed an object of investigation and has been the subject of many discussions between the supporters of the theory of slow ion discharge [1] and supporters of other hypotheses, e.g., the adsorption hypothesis [2]. Again, no satisfactory explanation has been found of the penetration of cathodic hydrogen into the inside of a metal, which has been investigated during recent years by, for example, Polukarov [3], Lihl [4], and Glikman and Snezhkova [5].

We have shown in our previous investigations [6] that interesting results, from the point of view of the mechanisms both of cathode processes and of hydrogen diffusion, may be obtained from observations on the extension of a fine wire used as cathode in the electrolysis of aqueous acid and alkaline solutions. The hydrogen atoms that penetrate inside the metal are the source of internal pressures and mechanical stresses, and these result in readily measurable changes in the length of the wire. It was shown that the change in length of a mild steel wire due to hydrogen uptake increased with the degree of recrystallization of the metal during cold working. It was shown by comparative mechanical tests that the value of the extending stresses arising in an iron cathode owing to saturation with hydrogen (in a solution of N sulfuric acid with an addition of thiourea or other substances that retard the recombination of hydrogen atoms to form molecules) probably attains 14 kg/sq. mm, which corresponds to a pressure of 1400 atm. It must be supposed that no less a pressure will arise at the phase boundary surface between the cathode and the electrolyte. When the solution contains no negative catalysts for the transition $2H \rightleftharpoons H_2$, the pressure will be generated mainly by molecular hydrogen, which cannot penetrate into iron, but in presence of substances that retard the above transition, the length of time during which H atoms exist in contact with the cathode surface will be increased, and this in its turn will result in a high partial pressure of atomic hydrogen, and in the penetration of this gas into the metal. Organic corrosion inhibitors, such as dibenzyl sulfoxide, are adsorbed on the cathode surface. This results in increase in the contact wetting angle at the boundary surface between cathode, electrolyte, and gas, and hence in increase in the size of the gas bubbles [7] and in reduction of the hydrogen pressure at the cathode surface. Such substances, therefore, retard the penetration of hydrogen into the metal.

EXPERIMENTAL

Principle of New Method of Investigating the Diffusion of Cathodic Hydrogen

In the course of studies relating to the deformations of iron cathodes due to hydrogen imbibition, it was found that a fine wire or ribbon bent in the form of the letter C straightens out in the manner of a Bourdon manometer tube as atomic hydrogen penetrates into it. Owing to the creation of high pressures in the internal inter- or intracrystal spaces of the material composing the cathode, forces are produced that tend to increase the radius of curvature of the bent cathode. The effect of these forces can be detected only in the case of objects of small cross-section that are capable of being saturated throughout with hydrogen under certain conditions, and are capable, in the case of annealed metal, of undergoing plastic deformation under the action of small stresses. This effect can be magnified by the use of a cathode made of wire bent in the form of a flat or cylindrical spiral.

Apparatus for measurements of this kind is shown in Fig. 1. The spiral cathode Fe was immersed in N sulfuric acid, and it was loaded at the lower end by the glass weight g, which, in its immersed condition, weighed about 4 g. The initial diameter of the turns of the spiral was 22 mm. In the experiments on the effect of current density and of the concentrations of arsenic and dibenzyl sulfoxide, the number of turns was $t = 14$, the initial length of spiral immersed in the solution was $l_0 = 50$ mm, and the total length of iron wire making up the spiral was $L = 1000$ mm. In the experiments on the effect of various catalyst poisons, the corresponding values were:

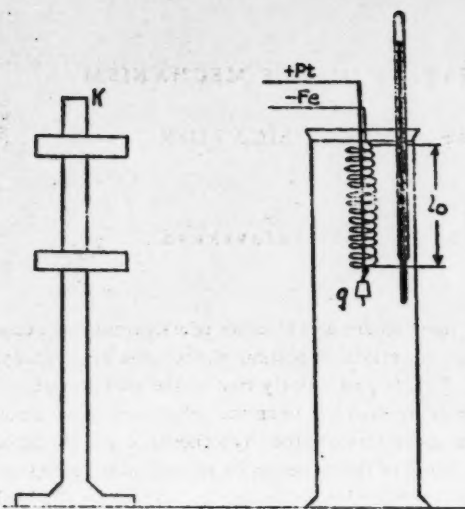


Fig. 1.

they were annealed in an atmosphere of hydrogen for 30 minutes at 900° in order to bring about recrystallization, removal of all stresses, and elimination of organic contamination from the surface of the wire. Each spiral was used for one measurement only.

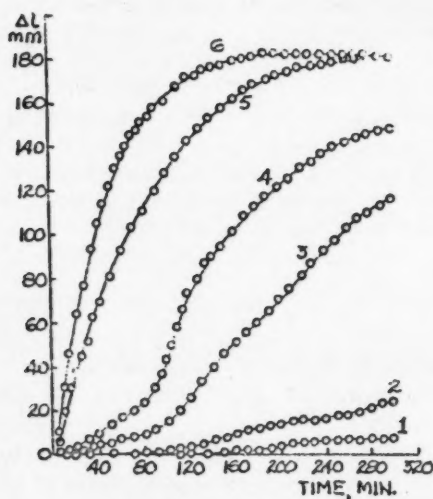


Fig. 2. 1 - 0.0015 mg/liter; 2 - 0.003 mg/liter; 3 - 0.0045 mg/liter; 4 - 0.06 mg/liter; 5 - 3.04 mg/liter; 6 - 30.4 mg/liter.

course of the penetration of hydrogen into the metal can be obtained. In Fig. 2 we show the results of observations on the extension of a spiral of $t = 14$ turns under the conditions required for imbibition of hydrogen at 20° and current density 0.018 amp/sq.cm in N sulfuric acid with additions of As_2O_3 at various concentrations. The time from the beginning of the electrolysis is given in minutes along the axis of abscissas, and the observed lengthening of the spiral is given along the axis of ordinates. Under Fig. 2, concentrations are given; they are expressed as milligrams of arsenic in one liter of acid. As will be seen from the course of these curves, increase in the concen-

$t = 7$ turns, $l_0 = 25$ mm, and $L = 500$ mm. Under the influence of cathodic polarization in presence of substances that retard the recombination of hydrogen atoms to form molecules, the radius of curvature of each turn of iron wire increased somewhat, so that the length of the spiral increased accordingly; the change in length of the spiral was measured with a cathetometer K provided with two reading telescopes.

The anode was either a straight platinum wire, diameter 1 mm, placed along the geometric axis of the iron spiral, as shown in Fig. 1, or a platinum gauze surrounding the spiral. The type of anode used did not affect the results.

Examples of the Application of the New Method

The investigation was carried out on an iron wire, diameter 0.45 mm, and having the following chemical composition (%):

C	Mn	P	S	Cu	Ni
0.09	0.35	0.028	0.048	0.47	0.03

The number of spirals necessary for carrying out a whole series of experiments were prepared, and

At the start of the investigations, the effect of temperature in the range 15-50° on the length of the spiral was determined. The spiral was immersed in distilled water, and was not polarized; under these conditions, no effects were observed. Experiment showed that the spiral did not undergo deformation under the influence of cathodic polarization in a solution of pure sulfuric acid; but if electrolysis occurred in the presence of certain elements of Groups V and VI of the periodic system that are known for their tendency to poison contact catalysts, the spiral lengthened rapidly, its movement being frequently observable by the unaided eye, and in some cases it attained a length of more than 1000% of the initial length of the spiral. These effects are irreversible, which is an indication of the plastic nature of the deformation.

The value of the change in length Δl of the spiral due to saturation with cathodic hydrogen must undoubtedly bear a quantitative relation to the value of the internal pressure of the gas accumulated within the structure of the metal; the change in length is established in experiments with satisfactory reproducibility, and hence, on the basis of measurements of the change in the length of the spiral, an idea of the

tration of arsenic from 0.0015 to 3 mg per liter results in a considerable acceleration of the untwisting of the spiral and the attainment of a high ultimate value of Δl corresponding to a definite final pressure of hydrogen accumulated within the wire.

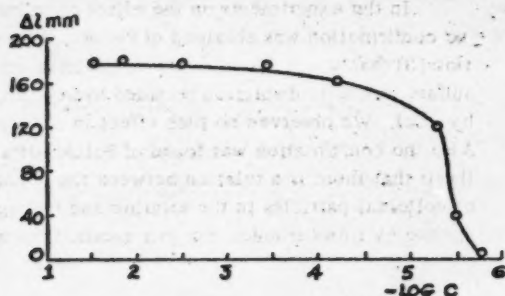


Fig. 3

used. As will be seen from the course of the curve in Fig. 5, dibenzyl sulfoxide at a concentration of 0.03 g/liter completely inhibits the hydrogen-diffusion process, but at higher concentration (above 0.05 g/liter) the inhibiting effect is reduced. This fact can be explained by the decomposition of dibenzyl sulfoxide molecules in the electrolysis. The measurements on the effect of the dibenzyl sulfoxide concentration, the results of which are given in Fig. 5, were carried out at a cathode current density of 0.018 amp/sq.cm. At higher current densities there was a displacement of the minimum of the curve toward higher dibenzyl sulfoxide concentrations.

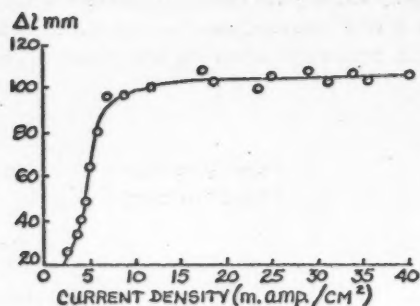


Fig. 4

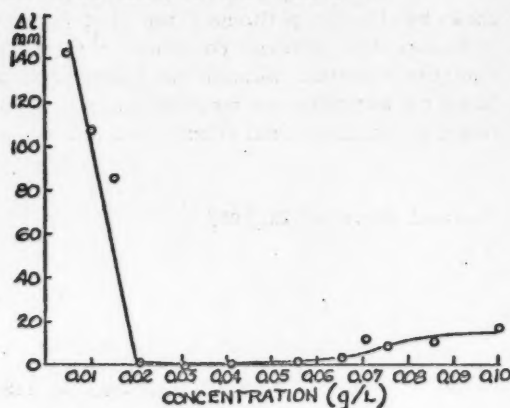


Fig. 5

Particularly interesting results were obtained in a comparison of the effects of various elements of Groups V and VI of the periodic system on the final value of the extension of the spiral (Fig. 6). These measurements were made on spirals for which the number of turns = 7. The cathode current density was 0.036 amp/sq.cm, and the temperature was 20°. The elements examined were Bi, Sb, As, and P (Group V) and Te, Se, and S (Group VI). Bismuth, selenium, tellurium, and antimony were added as oxides, sulfur as hydrogen sulfide, and phosphorus as phosphine. Sulfate and phosphate ions did not promote penetration of hydrogen into an iron cathode. Nitrogen, in the form of NH_4^+ or NO_3^- , also did not induce extension in the spiral cathode.

For all of these elements the dependence of Δl on the concentration was qualitatively similar to that found for arsenic (Fig. 3), but the position of the bend of the curve was different for each element. For all of these elements concentrations of greater than the limiting value were used. In Fig. 6 a comparison is made of the final values of the extension Δl , which are plotted against atomic number. In spite of a certain scatter in the results,

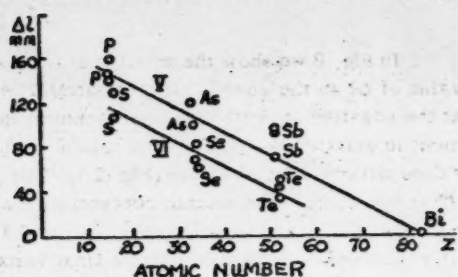


Fig. 6

a definite functional character is evident. Elements of Group V are in general more powerful in their action than those of Group VI, and in each group the activity falls as the atomic weight rises.

In the experiments on the effect of tellurium, no confirmation was obtained of Polukarov's observation [3] that the presence of sodium or magnesium sulfate in the acid solution retarded hydrogen imbibition by steel. We observed no such effect in our experiments. Also, no confirmation was found of Polukarov's hypothesis that there is a relation between the formation of colloidal particles in the solution and hydrogen uptake by iron cathodes, but this question requires further investigation.

SUMMARY

1. The behavior of spirals of iron wire during cathodic polarization indicates the suitability of the described method for the investigation of cathode processes, in particular for the investigation of the effect of the composition of the electrolyte and electrolysis conditions on the form in which hydrogen separates at the cathode.

2. The results of this investigation confirm the conclusions drawn from our previous work, which were that a high hydrogen pressure exists at the surface of a working cathode, the value of which is greatly dependent on the current density and on factors of an electrocapillary nature. In presence of traces of certain Group V and VI elements in the solution, the recombination of hydrogen atoms to form molecules is slowed down so that atomic hydrogen makes an appreciable contribution to the pressure acting on the cathode surface; this in its turn is the cause of the penetration of this gas into the structure of the iron.

3. The varying catalytic effects in the retardation of the recombination of hydrogen atoms into molecules shown by elements of Groups V and VI of the periodic system (Fig. 6) are probably associated with the varying stabilities of the hydrogen compounds of these elements. Nitrogen, which gives the stable compound NH_3 , has no catalytic properties; bismuth, the hydrogen compound of which is very unstable, shows a very slight tendency to retard the recombination reaction; but phosphorus, sulfur, arsenic, antimony, selenium, and tellurium greatly retard this reaction, their effectiveness depending on the valencies and atomic numbers of these elements.

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INVESTIGATION OF CATHODIC POLARIZATION OCCURRING DURING SIMULTANEOUS DISCHARGE OF IRON AND TUNGSTEN IONS

Z. A. Solovyeva and A. T. Vagramyan

The preparation of alloys of tungsten with various metals is a problem of great practical importance at the present time. Many papers have appeared on this problem during recent years. A review and detailed analysis of these papers up to 1940 has been given in an article by Sklyarenko and Druzhinina [1]. The most practical method appears to be the preparation of tungsten from aqueous solutions, and most of the papers, therefore, have been concerned with work in that direction.

The difficulty of preparing tungsten from aqueous solutions is associated with the preferential separation of hydrogen at the cathode owing to the strongly negative potential required for the separation of tungsten and the low value of the hydrogen overvoltage on tungsten. Among the investigations on the preparation of tungsten and its alloys from aqueous solutions, we must draw particular attention to the work of Golts and Kharlamov [2], who, in an investigation in 1936 on the polarization curves obtained in the deposition of tungsten-nickel, demonstrated the lowering of polarization in the deposition of nickel-tungsten, as compared with nickel alone; they showed also that the extent of this lowering increases with rise in temperature, and that this leads to increase in the tungsten content of the deposit.

Further work, by foreign investigators, on the preparation of tungsten alloys developed along the lines indicated by Golts and Kharlamov, namely, increasing of the depolarizing action of the metal codepositing with tungsten by rise in temperature, and addition of ammonium salts to the solution. The investigations on the preparation of tungsten alloys have been directed mainly to the selection of an electrolyte of suitable composition and a satisfactory electrolysis procedure, so as to obtain an alloy of high quality [3]. Very little study, however, has been devoted to the mechanism of the process of depositing electrolytic tungsten alloys. Recently, two papers by Holt and coworkers [4] on the mechanism of simultaneous discharge of ions of tungsten and metals of the iron group have appeared.

In these papers the theory of the so-called "catalytic reduction" of a metal was advanced. According to this theory, tungsten is reduced from aqueous solutions in presence of Ni, Fe, and Co as a result of the catalytic activity of the latter. Holt and Vaaler supposed that the following two reactions occur at the cathode:



Reaction 1 proceeds at the cathode until it is completely covered with a thin deposit of one of the iron-group metals, which encourages the occurrence of Reaction 2. When the iron-group metal (catalyst) has been covered by a layer of tungsten, Reaction 2 ceases and Reaction 1 proceeds again with the formation of a layer of catalyst.

In this way the periodic deposition of layers of iron-group metal (catalyst) and tungsten occurs at the cathode. The grounds for this point of view were found in polarographic investigations and in the investigation of the structure of electrolytic alloys carried out by Brenner, Burkhead, and Seegmiller [5]. In this connection, Holt and Vaaler point out that attempts to measure the potential for the electrodeposition of the alloy by the "direct" method do not give reproducible results. In a recent investigation, Clark and Lietzke showed that tungsten is deposited on a number of metals (Pb, Zn, Cd, Fe, Co, Ni, Cr, W, Cu, Ag, Pt), but the product of the electrochemical reaction is not the pure metal, but tungsten oxide. It was then noted that the largest amount of tungsten was separated in the case of metals of the iron group. The papers cited leave the following questions obscure:

1. Does the separation of tungsten occur as a result of "catalytic" reduction by hydrogen, or does depolarization occur as a result of the formation of a chemical compound or solid solutions between tungsten and the codepositing metal, as in the case of the discharge of sodium ions at a mercury cathode?

2. In the preparation of a tungsten alloy, is the discharge of the codepositing metal held back as a result of complex formation and leveling to the separation potential of tungsten?

For the investigation of alloy deposition we have used a direct method for the measurement of potentials that differs from the usual compensational method in the possibility of recording continuous change of potential of the electrode at any desired rate on photographic film.

EXPERIMENTAL

Method of Measurement

The potential of the electrode was measured with the aid of a high-resistance cathode voltmeter, taking a current of up to 10^{-12} amp, and a short-period mirror galvanometer having a sensitivity of 10^{-6} amp/mm and a period of 0.01 second. Such a method permits potential measurements to be made without the passage of appreciable current.

A 50-cc glass vessel was used as electrolytic cell. The cathode was formed by the end section of a copper or iron wire fused through the glass, the cathode surface being about 0.002 sq.cm; the anode was an iron or tungsten wire. A saturated calomel half-element was used as comparison electrode. The change in the potential of the electrode was recorded by means of the reflected light beam from the galvanometer on photographic film carried by a drum rotating at 1.5 mm per second.

Fig. 1 shows one of the records so obtained; it is a record of the change in the cathodic polarization of an iron electrode with time, the ordinates being potentials in millivolts and the abscissas time in seconds. The plot of the potential on the film was made as follows. A plot was first made of the zero position of the galvanometer, which corresponded to the potential of the calomel half-element to which all values of potential were referred. This line was plotted in a series of separate portions along the whole length of the film (lower, broken line). When the polarization current was switched on, the displacement of the reflection from the galvanometer from the zero line was a measure of the potential φ_1 for the separation of metal. For the determination of the stationary potential φ_0 of the electrode, the polarizing current was switched off after electrolysis had proceeded for a short time, and the position of the reflection from the mirror galvanometer after 15 seconds (sufficient time for the establishment of the potential) could be taken as a measure of φ_0 . The deflection of the galvanometer when the current was switched on for a second time corresponded to the potential for the separation on a freshly deposited one-component cathode surface. The overvoltage for the separation of metal is therefore expressed by the difference -

$$\eta = \varphi_1 - \varphi_0.$$

Experimental Results

In our study of the mechanism of the deposition of alloy, we first studied the cathodic polarization in citric acid solutions containing only iron ions or only tungsten ions, and then studied the simultaneous discharge of these ions. Following Holt, we used solutions containing, per liter, 66 g of citric acid, 50 g of Na_2WO_4 , 2 g of Fe^{++} and Fe^{+++} , and NH_4OH to pH 8-8.5.

Cathodic Polarization in the Electrolysis of Solutions Containing Iron Ions. In the investigation of the polarization of iron in citric acid solutions, its dependence on current density, temperature, and the charge of the iron ions was examined. Fig. 2 represents the variation in polarization with time in the electro-deposition of iron from citric acid solution at 25° and at a current density of 5 amp per sq.dm. It will be seen from Fig. 2 that the potential for the separation of iron under these conditions is 1093 mv (section on the left), the stationary potential for iron is 727 mv (middle section), and the overvoltage is 366 mv.

Effect of Temperature. Study of the polarization of an iron electrode has shown that the temperature of electrolysis has a great effect on the polarization and overvoltage during the separation of iron. The results of the investigation are given in Table 1; each experiment was done in duplicate. As will be seen from Table 1, the

TABLE 1

Temperature (°C)	Separation potential (mv)	Stationary potential of iron (mv)	Overvoltage at $i = 5$ amp/sq.dm, in mv
16	1067; 1095	690; 727	379; 366
70	948; 930	690; 690	253; 241

error in measurement is about 20-30 mv, for the necessity of finding place on 70-80 mm photographic film for a polarization of about 1000 mv makes it impossible to increase the sensitivity of the

measurement to more than 15-20 mv per 1-mm deflection of the galvanometer. It will be seen from Table 1 that raising of the temperature facilitates discharge of iron ions to the extent of 80-100 mv.

Effect of Current Density. The effect of current density on the polarization of iron was studied by the rapid method of recording polarization curves. Fig. 3 shows the polarization curve for the iron electrode, and it will be seen that the polarization does not vary linearly with current density. The form of the curve is analogous to the polarization curve for nickel obtained in sulfuric acid solutions [6]. According to the curve, the overvoltage at a current density of $i = 5$ amp per sq.dm is 374 mv. When the polarization curve is obtained at a different speed, the value of the polarization does not change, thus indicating the absence of concentrational polarization. The broken line in Fig. 3 is the stationary potential of iron at pH 8, which has the value 715 mv. As will be seen from the curve, after a short time the stationary potential is sharply displaced in the positive direction to a value corresponding to the potential of copper, which is the result of the autodissolution of iron in these solutions.

Cathodic Polarization in the Electrolysis of Solutions Containing Tungsten Ions. In the electrolysis of solutions containing only tungsten ions, i.e., in absence of a codepositing metal, no separation of tungsten could be detected, neither by analytical methods, nor by electrochemical methods, such as stationary potential measurements.

Cathodic Polarization in the Electrolysis of Solutions Containing Iron and Tungsten Ions. Study of the polarization in the simultaneous electrodeposition of iron and tungsten has shown that the separation potential for the alloy in citric acid solution at pH 8.1, at room temperature, and at a current density of $i = 5$ amp/sq.dm is 978 mv, the stationary potential of the alloy is 682 mv, and the overvoltage is 300 mv. The potential for the separation of the iron-tungsten alloy is, therefore, less than that for iron alone by about 120 mv.

It is impossible to compare the potential for the separation of the iron-tungsten alloy with that of pure tungsten, since we have not succeeded in causing the latter to separate from aqueous solutions, but in comparison with the standard potential of tungsten the separation potential for the iron-tungsten alloy (according to thermodynamical calculations) is depressed by 300 mv.

The effect of the electrolysis temperature on the polarization during electrodeposition of the alloy is shown in Table 2, from which it will be seen that raising of the temperature to 70° facilitates the separation of the iron-tungsten alloy to the extent of 100 mv.

TABLE 2

Temperature (°C)	Separation potential at $i = 5$ amp/sq.dm (mv)	Stationary potential at $i = 5$ amp/sq.dm (mv)
18	978	632
	978	672
70	879	628
	897	646

TABLE 3

Temperature (°C)	Depression of separation potential of alloy (mv) in comparison with -		$\frac{\Delta \phi W}{\Delta \phi Fe}$
	Standard potential of tungsten, $\Delta \phi W$	Separation potential of iron	
20	320	109	2.9
70	430	208	2.1

It will be seen from these results that the separation potential of iron at a current density of $i = 5$ amp/sq.dm, and at room temperature, is 1087 mv; at 70° it is 930 mv. The separation potential for the alloy, however, is 978 mv at 20° and 879 mv at 70°. The position is made clearer in Table 3, in which the lowering of the separation potential of the alloy with the respect to those of iron and tungsten is shown. It will be seen that the more positive the separation potential of the alloy, the less becomes the relative difference between the separation potentials of iron and tungsten. Rise in temperature, therefore, leads to a positive displacement in the separation potential of the alloy, and so increases the concentration of tungsten in the deposit.

Discussion of Results

In order to obtain an iron-tungsten alloy the separation potentials of the two components must be made to approach one another so that simultaneous deposition is possible. This can be attained in two ways: 1) raise the potential for the separation of the more positive metal (Fe) to that of the tungsten, for example, by complex formation; and 2) lower the separation potential of the more negative metal, for example, by formation of a chemical compound or solid solution.

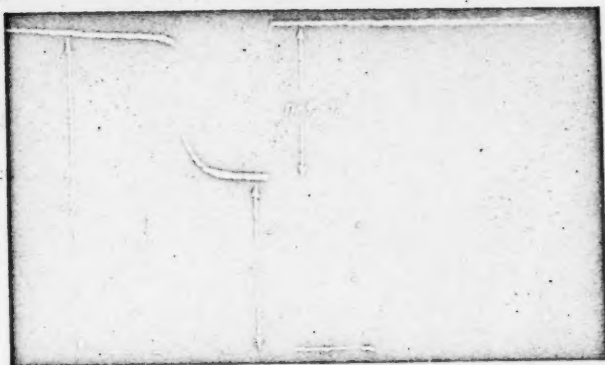


Fig. 1. Change of cathodic polarization with time, before and after switching off the current.

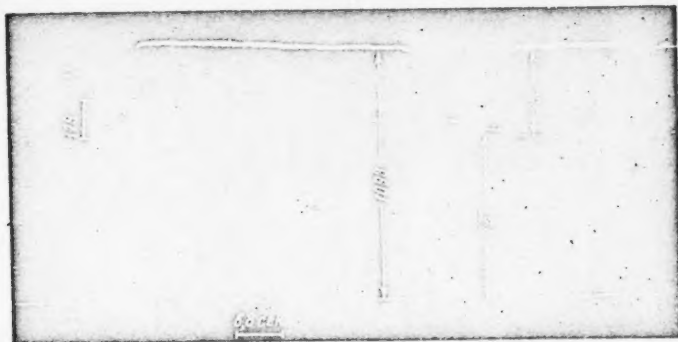


Fig. 2. Change of cathodic polarization with time in the electrodeposition of iron from citric acid solution at 25°C and at a current density of 5 amp/sq. dm.



Fig. 3. Variation of polarization with current density in the electrodeposition of iron (broken line: change in the potential of the electrode with time after switching off the current.)

The first way would not be satisfactory, for at a more negative potential of the electrode in aqueous solutions vigorous separation of hydrogen would occur. The second way is the more expedient, but it must be remembered that the work of formation of the chemical compound must be sufficiently large, in order to make the separation of tungsten possible.

We have already pointed out that, according to Holt and his students, the first stage in the electrodeposition of alloy is the separation of an iron-group metal on the electrode, after which separation of a layer of tungsten occurs on the surface of the catalyst. Holt, unfortunately, does not discuss the mechanism of the catalyzing action of the iron-group metal. In confirmation of his theory, he refers to the photomicrographs of sections taken by Brenner. From the photomicrographs, however, it may be seen that the thickness of individual layers is about $1\ \mu$.

If alternate deposition of tungsten and iron does occur on the cathode, then a periodic variation in the potential should occur, for the potential of the electrode should have a higher value during the separation of an iron-group metal, and then fall by about 100 mv during the separation of the alloy. The period with which the potential would vary would be appreciable, for the deposition of a layer visible on the photomicrographs (X 250) to which Holt refers would require several seconds.

However, as our experiments on the variation of polarization with time have shown, no such variation of potential during electrodeposition of alloy occurs. It is impossible, therefore, to treat the layered structure of the electrolytic deposit that is visible on microsections as the result of the periodic deposition of two metals, all the more since a similar layered structure can be observed in the electrodeposition of a single metal.

It appears more likely that we are concerned here with the same mechanism of deposition as that found in the separation of sodium at a mercury cathode, where as a result of the formation of a chemical compound the potential required for the discharge of a sodium ion is greatly reduced. In the deposition of tungsten alloys, we probably again have the formation of a chemical compound (of the type Fe_2W), and the discharge of tungsten ions is, therefore, greatly facilitated, and the potential required for its separation becomes even less than the standard tungsten potential. The difference lies in the fact that in the electrolytic deposition of tungsten alloys, simultaneous separation of iron and tungsten occurs with formation of an alloy and periodic variation in potential therefore does not occur.

SUMMARY

1. An investigation of the simultaneous deposition of iron and tungsten has shown that the separation potential for the alloy is 100 mv less than the separation potential for iron and 300 mv less than the standard potential of tungsten.
2. It has been shown that the possibility of discharging tungsten ions depends on the depolarizing action of the simultaneous discharge of iron and tungsten ions.
3. It has been shown also that there is no periodic variation in the potential during the electrodeposition of tungsten and iron; which is in conflict with Holt's ideas on the layered deposition of iron and tungsten.

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REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 2. REACTION OF VITREOUS SODIUM DISILICATE WITH AQUEOUS SOLUTIONS

Yu. A. Shmidt

In the previous paper we described the reaction of vitreous sodium silicates with water and hydrochloric acid solutions [1]. In the present communication we describe a more detailed study of the reaction of vitreous sodium disilicate with various aqueous solutions.

EXPERIMENTAL

We have already described the experimental procedure [1]. For the characterization of the processes occurring, we make use of the following quantities: $n_{\text{Na}_2\text{O}}$ and n_{SiO_2} , the amounts in moles per sq.cm of the respective oxides passing from the glass into solution; $v_{\text{Na}_2\text{O}}$ and v_{SiO_2} , the mean rates of the passage of these oxides into solution (molc/sq.cm/min); δ , the thickness of the siliceous film on the surface [1].

In the experiments at 40°, in addition to agitation of the solution with a stirrer, we tried also vigorous shaking (about 1000 shakes per minute) of the sample in the liquid, which aided in the effective removal from the surface of soluble products of the reaction of the glass with the solution. At the beginning of an experiment agitation by shaking resulted in an increase of about 50% in the rate at which Na_2O passed into solution, but later (after one hour) the rate was found to be about the same as that found in the experiments with a stirrer. It may be supposed from this that at the beginning of the experiment an alkaline diffusion layer was formed on the surface of the glass, but later the concentration of alkali at the surface fell and approached the concentration in the solution. More vigorous removal of alkali from the surface by means of shaking led to a reduced value of v_{SiO_2} , the reduction being particularly marked at the beginning of the experiment. In other respects the observed behavior was similar to that observed when agitation was effected with a stirrer.

In order to study the effect of temperature, experiments were carried out at 25°, 55°, 70°, and 100°; the results are given in Table 1. The variation of the values of $v_{\text{Na}_2\text{O}}$, v_{SiO_2} and δ with time is shown in Figures 1 and 2. At 25° and 40° the main process is the leaching of the glass, leading to the formation of a residual siliceous film, the thickness of which grows continuously. With rise in temperature the rate of the passage into solution of the components of the glass, particularly silicic acid, rises rapidly, but as the alkali concentration in the solution increases very rapidly in the experiments at 55° and 70°, the thickness of the residual film, having attained a definite limit, begins to decrease. For this reason, the value of $v_{\text{Na}_2\text{O}}$, which falls at the beginning of these experiments, then begins to rise. The variation with time of the rate of passage of silicic acid into solution is expressed by curves having maxima that become more marked as the temperature rises, simultaneously moving toward the axis representing the beginning of the experiment.

When vitreous sodium disilicate reacts with water, the concentration of alkali in the solution increases, i.e., there is an increase in the sodium ion concentration, and a reduction in the hydrogen ion concentration. In order to study the effect of variation in the concentration of these ions on the course of the process, experiments were carried out on the reaction of sodium disilicate with 0.01 N, 0.1 N, and N solutions of sodium chloride, and also with 0.01 N solutions of hydrochloric acid and caustic soda. The results of these experiments, which were carried out at 40°, are shown in Figures 3 and 4. With increase in the sodium chloride concentration, and also with decrease in the hydrogen ion concentration, the value of $n_{\text{Na}_2\text{O}}$ falls somewhat, and that of n_{SiO_2} , on the contrary, rises greatly. Check determinations of the silicic acid in the solution after preliminary heating of it with alkali showed that in all experiments the silicic acid passed into solution in a molecular, or almost molecular, degree of dispersion.

Weighing of the samples before and after the experiment showed that their loss in weight was less than the weight of components found in the solution by analysis. After drying, the surfaces of the samples were covered with cracks. All this points to the presence of water in the surface layer. The calculated amount of water as percent by weight of the silica remaining in the surface layer was about 30. The experiments at 70° and 100° formed an exception: the process occurring amounted to dissolution of sodium disilicate. In this case the loss in weight of the samples coincided with the weight of components found in the solution by analysis, and the dried surfaces of the samples were unchanged in appearance.

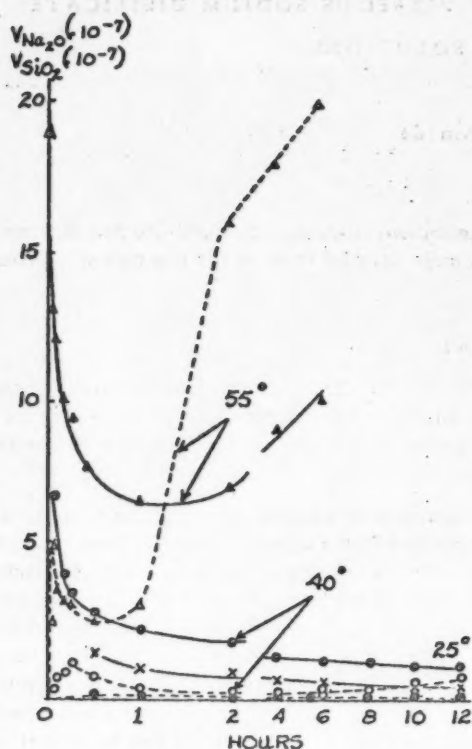


Fig. 1. Variation with time of the rate (mole/sq.cm) of the passage of Na₂O and SiO₂ into solution:

— V_{Na₂O}; - - - V_{SiO₂}

In further experiments sodium disilicate powder having a grain size of 140-200 μ was given a full treatment with 0.01 N hydrochloric acid. After being dried in the air at room temperature, it was found to have the following composition: SiO₂ - 81.2%; Na₂O - 0.54%; H₂O - 18.3%. Similar treatment of sodium disilicate filaments, diameter about 100 μ, led to an increase of about 10% in thickness. Hence, in spite of its appreciable water content, the siliceous film formed on the surface of sodium disilicate apparently undergoes very little swelling.

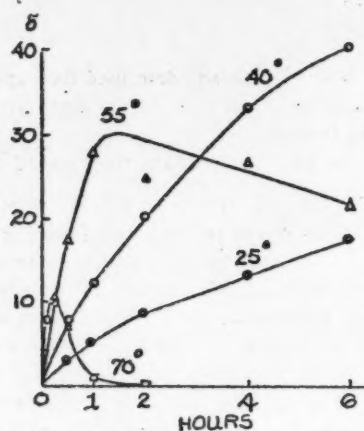


Fig. 2. Variation with time of the thickness of the residual siliceous film δ (in microns) at various temperatures.

Discussion of Results

As indicated in the previous paper, the primary process in the interaction of sodium silicates with water is the exchange reaction between the sodium ions of the glass, and the hydrogen ions in the solution:



It is known from experiment that ion exchange between the surface of a solid (in particular, glass) and a solution proceeds at a high velocity [2,3, 4]. An equilibrium state is, therefore, reached rapidly, and the ion concentrations in the solid phase at its boundary with the solution are then determined by the composition of the solution, in accordance with the ion-exchange law [5]. The exchange of ions between glass and solution forms the basis of Nikolsky's theory of the glass electrode [6], which has been confirmed in a number of later investigations [7, 8, 9]. The theory of the glass electrode examines ion exchange at the boundary between glass and solution under equilibrium conditions, and does not concern itself with processes associated with the breakdown of the glass. In the study of the kinetics of the interaction of glass with water, the observed phenomena are more complex, for, in addition to the ion-exchange process, the diffusion of the ions in the solid and liquid phases, and the variation of the thickness of the residual siliceous film with time begin to play a part. When vitreous sodium disilicate inter-

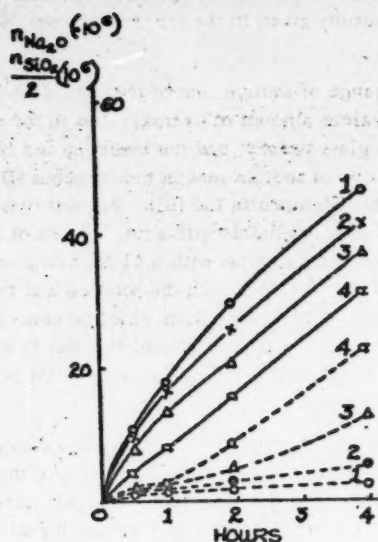


Fig. 3. Interaction of vitreous sodium disilicate with sodium chloride solutions: 1 - water; 2 - 0.01 N NaCl; 3 - 0.1 N NaCl; 4 - 1.0 N NaCl;

— $\frac{n_{Na_2O}}{2}$; - - - $\frac{n_{SiO_2}}{2}$

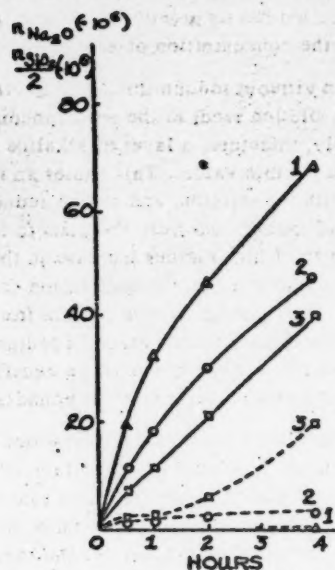


Fig. 4. Interaction of vitreous sodium disilicate with solutions of hydrochloric acid and of caustic soda: 1 - 0.01 N HCl; 2 - water; 3 - 0.01 N NaOH;

— $\frac{n_{Na_2O}}{2}$; - - - $\frac{n_{SiO_2}}{2}$

acts with water, a siliceous film immediately forms on its surface as a result of the exchange of sodium ions of the glass with hydrogen ions of the solution. In this case, therefore, the passage of sodium ions (exchanging with hydrogen ions) from the glass to the solution is made up of a number of processes:

1. Diffusion of Ions in the Siliceous Film. The rate of diffusion is determined by the thickness of the siliceous film, the difference in concentration of sodium ions, and the diffusion coefficient for ions in the film. The last depends on the nature of the exchanging ions and the structure of the film.

2. Passage of Ions from the Surface of the Film to the Solution. On the basis of data available in the literature, it may be supposed that the passage of ions from the surface of the film to the solution proceeds fairly rapidly, in comparison with diffusion processes; as a result, the concentration of ions in the film at its boundary with the solution, if not at the equilibrium value, tends to approach that value.

3. Diffusion of Ions in Solution. The rate of this process depends mainly on the diffusion coefficient for ions in the solution, and the difference in the alkali concentration at the surface and in the solution.

The formation of a siliceous film on the surface retards the passage of sodium ions into the solution to an appreciable extent. This indicates that in this case the slowest stage - the rate-determining stage for the whole process - is the diffusion of ions in the film. The rate of this diffusion depends on the difference of sodium ion concentration within the film. Since the sodium ion concentration at the boundary between unchanged glass and the film is constant, this difference is determined by the value of this concentration at the boundary between the film and the solution. The latter, in its turn, is related to the composition of the solution by the equation of the ion-exchange law:

$$\frac{a_{H^+} \cdot a'_{Na^+}}{a_{Na^+} \cdot a'_{H^+}} = K,$$

(a_{H^+} and a_{Na^+} are the activities of the ions in the solution; a'_{H^+} and a'_{Na^+} are their activities in the siliceous film at its boundary with the solution [6]).

It is known from experiments with a glass electrode that the value of the constant K for glasses that do not contain boric anhydride or aluminum oxide is very small. In an acid medium, therefore, the sodium ion concentration in the film at its boundary with the solution is close to zero, so that the difference in this concentration within

the film has its greatest value and is practically independent of the hydrogen concentration in the solution. As a result, in spite of the great thickness possessed by the film in this case, the rate of passage of sodium ions from glass to solution has its greatest value and, as can be seen from the results given in the preceding paper, does not depend on the concentration of acid.

When vitreous sodium disilicate interacts with water, the exchange of sodium ions of the glass with hydrogen ions of the solution leads to the simultaneous appearance of an equivalent amount of hydroxyl ions in the solution. Immediately, therefore, a layer of alkaline solution is formed at the glass surface, and the hydrogen ion concentration falls to a negligible value. This causes an increase in the concentration of sodium ions in the siliceous film at its boundary with the solution, and so to a reduction in the concentration difference in the film. For this reason the rate of passage of sodium ions from the glass to the solution is lower than in experiments with acid, in spite of the lower thickness of the film. Further increase in the alkalinity of the solution (experiments with 0.01 N caustic soda) lead to still greater increase in the sodium ion concentration in the film at its boundary with the solution and to reduction in the rate of the passage of sodium ions from the glass to the solution. Increase in sodium chloride concentration also reduces the rate of the passage of sodium ions from glass to solution. The explanation of this lies in the fact that, as can be seen from the ion-exchange equation, with increase in the concentration of sodium ions in the solution, their concentration in the film at its boundary with the solution also increases.

An important effect on the interaction of sodium disilicate with water is exerted by the change during the experiment in the thickness of the surface siliceous film. At the beginning of the process, as a result of the small thickness of the film, the rate at which sodium ions pass into the solution is high, so that a high concentration of alkali is immediately formed at the surface. As the thickness of the film increases, the rate at which sodium ions pass into the solution diminishes. At the same time the alkali concentration at the surface is also reduced and approaches the concentration in the bulk of the solution. As, however, the latter concentration increases constantly, the alkali concentration in the solution, interacting with the surface, may again begin to increase as the experiment proceeds further. In a number of cases this increase leads to intensified dissolution of the residual film and to decrease in its thickness, and there is a consequent increase in the rate at which sodium ions pass into the solution.

TABLE 1
Effect of Temperature on the Interaction of Vitreous Sodium Disilicate with Water

Temp. (°C)	Indexes	Time									
		(minutes)						(hours)			
		1	2.5	5	10	15	30	1	2	4	6
25	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	—	—	—	—	—	4.6	7.6	13	20	26
	$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	—	—	—	—	—	0.2	0.6	1.2	2.1	2.6
40	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	—	1.7	2.8	4.9	6.6	11	18	30	47	62
	$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	—	0.07	0.25	0.66	1.2	2.3	3.2	4.2	5.8	9.3
55	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	1.9	3.9	7.0	12	17	28	48	90	202	317
	$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	0.26	1.1	2.0	3.6	5.2	9.2	19	112	328	570
70	$\bar{n}_{\text{Na}_2\text{O}} \cdot 10^{-6}$	4.8	11	22	43	64	138	310	643	—	—
	$\bar{n}_{\text{SiO}_2} \cdot 10^{-6}$	5.2	11	23	57	100	256	614	1290	—	—

Note. At 100° the values of $\bar{n}_{\text{Na}_2\text{O}}$ and \bar{n}_{SiO_2} (for one hour) are respectively $3200 \cdot 10^{-6}$ and $6400 \cdot 10^{-6}$ mole/sq.cm.

With rise in temperature, the rate at which the components of the glass pass into solution increases considerably. A comparison of values of $\bar{v}_{\text{Na}_2\text{O}}$ at various temperatures, but for approximately identical film thicknesses, shows (Table 2) that the rate, and therefore coefficient, of diffusion in the film increases by 7-10% for every degree rise in temperature. Hence, the diffusion coefficient in the film varies with temperature according to a law that is characteristic for solids. This conclusion is in agreement with what we have pointed out above; namely, that the siliceous film on the surface of vitreous sodium disilicate contains 70-80% of SiO_2 and differs little in volume from the original glass.

TABLE 2

Comparison of Values of v_{Na_2O} at Various Temperatures

Temp. (°C)	Time	δ (microns)	$\frac{v_{Na_2O}}{(10^{-7})}$	Temp. (°C)	Time	δ (microns)	$\frac{v_{Na_2O}}{(10^{-7})}$	$\frac{v_{Na_2O}}{v_{Na_2O}}$	Increase in $\frac{v_{Na_2O}}{(\%/1^\circ)}$
25	30 min	3.3	1.5	40	10 min	3.4	4.2	2.8	7.1
	4 hr	14	0.6		1 hr	13	2.4	4.0	9.8
40	2.5 min	1.2	6.8	55	1 min	1.3	19	2.8	7.1
	15 min	4.4	3.4		5 min	4.4	12	3.5	8.8
55	5 min	4.4	12	70	2.5 min	4.0	41	3.4	8.6

The diffusion coefficient of alkali in solution depends little on the temperature, rising only by 2.4% per degree rise in temperature [10]. Hence, the relative increase in the diffusion coefficient in the film with rise in temperature is considerably greater than the relative increase in this coefficient in the solution, so that the alkali concentration in the solution at the glass surface must increase with rise in temperature. It will not, however, approach saturation. If such saturation were to occur, the slowest stage of the process would be the diffusion of alkali in the solution, and the increase of v_{Na_2O} with temperature would be considerably less than that which is observed in practice.

These considerations enable us to explain qualitatively the effect of temperature on the interaction of sodium disilicate with water and, in particular, the variation in the form of the maxima on the curves showing the dependence of v_{SiO_2} on time at various temperatures. It will be seen from the course of the curves in Fig. 1 that during the first moments of interaction, the rate at which Na_2O passes into solution, and hence the alkali concentration at the surface, is very great. In spite of this, the rate at which silicic acid passes into solution in experiments at 25-55° during the first moments of interaction is zero. This indicates that the dissolution of silicic acid is a considerably slower process and lags behind the transfer to the solution of the corresponding amounts of Na_2O . In the succeeding period the rate at which silicic acid passes into the solution gradually increases. This increase, of course, is the more rapid, the higher the alkali concentration in the surface layer of solution. As we have seen, increase in this concentration is encouraged by rise in temperature.

In the experiments at 25°, the ratio of the diffusion coefficients in the film and in the solution was apparently such that the initial alkali concentration at the surface was relatively low, so that the rate at which silicic acid passed into the solution increased comparatively slowly at the beginning of the experiment and was low in absolute value. The growth in the thickness of the film was also relatively slow. As a result, the reduction in the alkali concentration at the surface proceeded more slowly than in the experiments at higher temperatures. Owing to these circumstances the maximum on the curve of v_{SiO_2} against time is attained relatively late and is not strongly marked.

With rise in temperature the initial alkali concentration at the surface increases considerably. At the same time, the rate at which the thickness of the film increases also rises with rise in temperature, leading to a more rapid relative decrease in the alkali concentration at the surface. As a result, the rate at which silicic acid passes into solution at the beginning of the experiment increases at an increasing rate as the temperature rises and attains greater and greater absolute values, though its relative diminution begins more and more early.

The second increase in the rate at which silicic acid passes into solution, which is observed in the experiments at 40-70°, is caused by the increase in concentration of alkali in the main bulk of the solution, which in time overcomes the effect of the reduction in concentration at the surface that occurs at the beginning of the experiment.

With rise in temperature, the rate at which silicic acid passes into solution increases to a considerably greater extent than v_{Na_2O} . This is to be explained by the sharp increase in the alkali concentration of the solution (both at the surface, and in the body of the solution), and also by the fact that rise in temperature facilitates the breaking of the bonds between the silicon-oxygen groups forming the skeleton of the film. As a result, the leaching of the surface with formation of a siliceous film is replaced as the temperature rises by complete dissolution of this film and hence of the whole of the glass.

The rate at which silicic acid passes into solution depends not only on the temperature, but also on the initial composition of the solution: an increased rate is favored by rise in concentration not only of alkali, but also of sodium chloride. In an acid medium, the presence in the solution of an excess of hydrogen ions prevents the formation of alkali at the surface, and for this reason, the amount of silicic acid passing into solution is much less in this case than in the others.

As in the previous investigation, our results suggest that the formation of the siliceous film occurs by the exchange of sodium ions for hydrogen ions in the surface layer of glass. Together with these hydrogen ions, some water penetrates into the surface layer. In all probability, the exchange of sodium ions for hydrogen ions does not result in the breakdown of the bonds present in the glass between the silicon-oxygen tetrahedra, but it undoubtedly has a considerable effect on the state of the surface layer. This is evident from the fact that the same factors that cause an increase (at the expense of hydrogen ions) in the sodium ion concentration in the film at its boundary with the solution also favor the passage of silicic acid into the solution. All our results indicate the dissolution of the siliceous film to be a secondary process occurring by the gradual breaking away of individual silicon-oxygen groups from the surface.

SUMMARY

1. The rate at which sodium ions pass into solution when there is a siliceous film on the surface of vitreous sodium disilicate is determined by the diffusion of the ions in this film.
2. Increase in the sodium ion concentration and decrease in the hydrogen ion concentration of the solution retards the diffusion of sodium ions in the film. At the same time, the rate of the dissolution of the film, which is a secondary process, increases.
3. With increase in temperature, the rate of the diffusion of sodium ions in the film rises greatly. The rate of the dissolution of the siliceous film rises still more, so that with rise in temperature the leaching of the surface of vitreous sodium disilicate is replaced by the complete dissolution of the glass.

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REACTION OF VITREOUS SODIUM SILICATES AND ALUMINOSILICATES WITH AQUEOUS SOLUTIONS

COMMUNICATION 3. EFFECT OF THE ADDITION OF SILICA AND ALUMINA TO SODIUM SILICATES ON THE INSTABILITY OF THE LATTER TO ACIDS

S. K. Dubrovo

From a study of the nature of the breakdown of silicate glasses under the action of chemical reagents, Grebenshchikov concluded that glass contained a strong silica skeleton, consisting of silica that was not combined with basic oxides [1]. Such a skeleton can be represented as an array of SiO_4 groups (silicon-oxygen tetrahedra) in space. Silicon-oxygen tetrahedra in which the apexes are associated with alkali or alkaline-earth ions form weak, vulnerable links in the skeleton. With increase in the relative number of such groups, the passage of silica into the solution as anions or small aggregates also increases. When alumina is introduced into the composition of vitreous sodium silicates, these glasses undergo radical changes.

As is well known, Vernadsky, in developing the theory of complex siliceous anhydrides and their derivatives, introduced the concept of the identity in the functions of silicon and aluminum in many natural aluminosilicates [2]. This was later confirmed by X-ray analysis for important minerals, such as feldspar, in which it was established that a skeleton built of alternating SiO_4 and AlO_4 groups was present. In such compounds, therefore, aluminum has a coordination number of four [3]. On the other hand, in some minerals aluminum has a coordination number of six, being a structural analog of magnesium (mica, cyanite, etc.). The variation of the coordination number of aluminum in minerals is reflected in their physical properties [4]. This has served as a basis for the study of the state of aluminum in glasses. A number of investigators have established, with the aid of determinations of refractive index, density, and other physical properties, that in alkaline aluminosilicate glasses aluminum has a coordination number of four and is a structural analog of silicon [5, 6]. In view of these findings, in the study of the interaction of vitreous sodium aluminosilicates with aqueous solutions, it is necessary to pay particular attention to the peculiar features introduced by aluminum when it enters the skeleton of glass.

The aluminum-oxygen tetrahedron AlO_4 has, in comparison with the silicon-oxygen tetrahedron, an excess negative charge, which is compensated by a sodium ion. This in itself leads to increase in the number of mutually bound silicon-oxygen groups when Al_2O_3 is introduced into the composition of sodium silicates. At the same time there is a reduction in the number of Si-O-Si linkages, owing to the appearance of silicon-oxygen tetrahedra bound at certain apexes to aluminum-oxygen tetrahedra, so that in the skeleton of an aluminosilicate glass depolymerization of silica occurs. It is probable, however, that this depolymerization has a detrimental effect on the strength of the skeleton apparently only in the case of interaction with reagents that selectively leach out aluminum ions; for example, solutions of mineral acids (except hydrofluoric). When a relatively large number of silicon-oxygen groups are bound to aluminum-oxygen groups, then discontinuities will be formed in the skeleton of the glass when the latter are washed out. The residual groups (SiO_4) are isolated, and, being small aggregates, have enhanced solubility in acids. For certain $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in vitreous sodium aluminosilicates, complete dissolution of the glass may occur, no residual layer being formed. In the course of time, depending on the pH of the reacting medium and the concentration of silicic acid in solution, the latter may polymerize, and then coagulate, which is a secondary process. In considering the effect of Al_2O_3 on the properties of vitreous sodium silicates, it is of course necessary to take into account not only the change in the strength of the skeleton of the glass, but also the strength of the electrovalent bonds formed with sodium ions.

In order to obtain a more complete picture of the mechanism of the breakdown of vitreous sodium aluminosilicates under the action of chemical agents, it is desirable to characterize their stability by the individual amounts of the components of the glass passing into the solution. Thus the results of Dimpleby and Turner's experiments [7] on the chemical stability of sodium aluminosilicates are not as valuable as they might be, since the stability is measured by the loss in weight of glass powders when boiled with various reagents, and it is not possible to form an idea of the proportions of the components of the glass passing into solution and so of the extent to which the skeleton of the glass is broken down. Other papers that have appeared in this field are concerned mainly with the more complex sodium calcium aluminosilicates, which we shall not consider here.

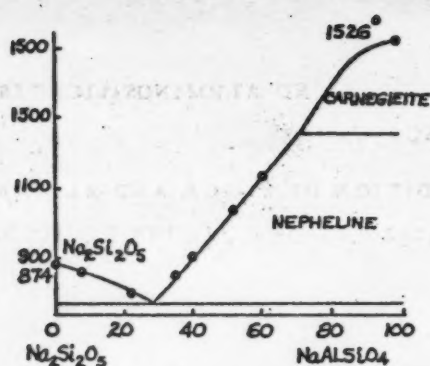


Fig. 1. The sodium disilicate - nepheline section of the phase diagram of the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (the positions of the investigated aluminosilicates are shown by points).

silicate glasses, we used sodium carbonate (pure for analysis), aluminum hydroxide (chemically pure) containing 65.5% Al_2O_3 , and ground quartz (containing not more than 0.2% of impurities). The glass was prepared in a platinum crucible at 1400-1500° in a furnace having silt resistors; stirring was performed mechanically with a platinum stirrer. The method of preparing and preserving the samples was the same as in the case of vitreous sodium silicates [8]. The annealing was carefully checked by means of a polariscope. The majority of the investigated glasses were analyzed, and their compositions (according to synthesis and by analysis) are given in Table 1.

TABLE 1

Compositions of the Sodium Aluminosilicates Investigated

Molecular proportions			Composition according to synthesis						Composition by analysis			Annealing temp. (°C)
Na ₂ O	Al ₂ O ₃	SiO ₂	(mole %)			(wt %)			(wt %)			
			Na ₂ O	Al ₂ O ₃	SiO ₂	Na ₂ O	Al ₂ O ₃	SiO ₃	Na ₂ O	Al ₂ O ₃	SiO ₂	
1	0.05	2	32.8	1.6	65.6	33.1	2.7	64.2	—	—	—	490
1	0.15	2	31.7	4.8	63.5	31.4	7.8	60.8	—	—	—	510
1	0.30	2	30.3	9.1	60.6	29.2	14.4	56.4	29.2	14.5	56.2	520
1	0.40	2	29.4	11.8	58.8	27.8	18.3	53.9	27.7	18.1	53.7	530
1	0.50	2	28.6	14.3	57.1	26.6	21.9	51.5	26.6	21.7	51.4	540
1	1.0	2	25.0	25.0	50.0	21.8	35.9	42.3	22.3	36.3	41.9	
	Natural nepheline		—	—	—	—	—	—	19.4	34.8	43.3	
	Vitreous nepheline		—	—	—	—	—	—	21.0	34.9	43.4	

2. Procedure. The experiments were carried out in quartz apparatus at $40 \pm 0.5^\circ$ in an air thermostat having a bimetal thermoregulator. The method of testing the aluminosilicates was essentially the same as that used for sodium silicates, and we have described this previously [8]. The amounts of the components passing into solution were determined by colorimetric methods. Sodium was separated by means of zinc uranyl acetate, dissolved in acetic acid, and estimated colorimetrically after addition of potassium ferrocyanide (the compound formed by ferrocyanide and potassium uranyl acetate, in amount equivalent to the sodium in the solution, is of a brown color). Silicic acid was determined in solution either as the yellow complex formed with ammonium molybdate, or as molybdenum blue, the reduction product of the yellow complex. The amount of Al_2O_3 in the solution was determined by means of aluminon [9], or, when large amounts were present, the gravimetric hydroxyquinoline method was used also, the method being modified as described by us for the determination of Al_2O_3 in presence of silicic acid [10]. The amounts found by analysis for all of the components of the glass present in the solution were then recalculated as moles of the corresponding oxides passing into the solution per sq.cm of the surface of

In sodium aluminosilicates, as in sodium silicates, there first occurs breakdown in the O-Na bond owing to exchange of sodium ions with hydrogen ions of the reacting solution, so that a residual aluminosiliceous layer is formed on the surface of the glass. Aluminum ions are also apparently able to undergo exchange with hydrogen ions.

In the present paper we give the results of an investigation of the course and the character of the breakdown undergone by vitreous sodium aluminosilicates in 0.1 N hydrochloric acid. In the first place, we have studied aluminosilicates whose compositions fall on the disilicate-nepheline section of the phase diagram of the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Fig. 1).

EXPERIMENTAL

1. Preparation of Vitreous Sodium Aluminosilicates. For the preparation of aluminosilicates.

the sample, which were denoted respectively as $n\text{Na}_2\text{O}$, $n\text{Al}_2\text{O}_3$, and $n\text{SiO}_2$.

For the characterization of the interaction of vitreous sodium silicates with aqueous solutions, we have previously made use also of the quantity α , which expresses the fraction of the silicic acid in the reacting layer of glass that passes into solution. In the case of sodium aluminosilicates, we make use of a further analogous quantity β , which expresses the fraction of the alumina present in the attacked layer that passes into solution. Thus, $\beta = \frac{n\text{Al}_2\text{O}_3}{k \cdot n\text{Na}_2\text{O}}$, where k is the number of moles of Al_2O_3 entering into the composition of the glass expressed in the form $\text{Na}_2\text{O} \cdot k \text{Al}_2\text{O}_3 \cdot m\text{SiO}_2$. Comparison of the values of α and β gives a clear picture of the mechanism of the breakdown of the glass and the change in the composition of the residual surface layer.

3. Interaction of Sodium Aluminosilicates with 0.1 N Hydrochloric Acid. We have investigated the stabilities of six vitreous sodium aluminosilicates in 0.1 N hydrochloric acid. Each of the investigated samples of aluminosilicates can be regarded in two ways: either as sodium disilicate to which a certain amount of Al_2O_3 has been added, or as a silicate in which part of the SiO_2 has been replaced by Al_2O_3 , it being assumed that aluminum is here a structural analog of silicon, when 1 mole of SiO_2 is equivalent to 0.5 mole of Al_2O_3 . Hence, when we wish to compare the effects of the contents of SiO_2 and Al_2O_3 in sodium silicates on their stabilities, it is necessary to compare the glasses that can be treated as silicates having additions of SiO_2 and Al_2O_3 in the given proportions.

We have investigated also the action of hydrochloric acid on natural nepheline and on the vitreous product obtained by melting nepheline at 1520° . The nepheline glass was annealed and then sawed into samples with the form of a parallelepiped. In the trials on crystalline and vitreous nepheline and on vitreous sodium aluminosilicate of composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, polished samples were used, whereas the remaining samples had fire-polished surfaces.

Natural nepheline does not belong quite strictly to the sodium disilicate series, for it contains rather too much silica and about 0.6% of extraneous materials. The molecular proportions of the oxides present are, however, found by analysis to be close to those of an aluminosilicate of composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, so that we considered it desirable to determine its stability under the same conditions. Also, it was considered to be of interest to compare the stabilities of vitreous and crystalline samples having the same composition, as we have previously done in the case of feldspars [11].

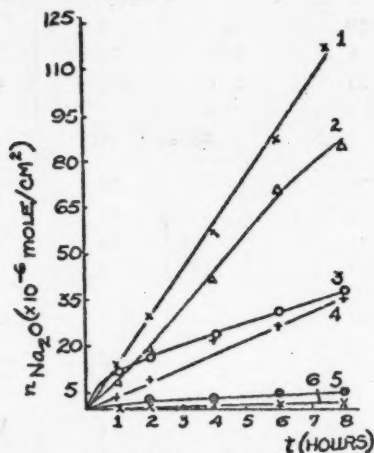


Fig. 2. Interaction of sodium aluminosilicates with 0.1 N hydrochloric acid at 40° : 1 - $\text{Na}_2\text{O} \cdot 0.4 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; 2 - $\text{Na}_2\text{O} \cdot 0.5 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; 3 - $\text{Na}_2\text{O} \cdot 0.05 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; 4 - nepheline glass; 5 - $\text{Na}_2\text{O} \cdot 0.15 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; 6 - $\text{Na}_2\text{O} \cdot 0.30 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.

residual protective layer, therefore, was enriched in silica. From a glass of composition $\text{Na}_2\text{O} \cdot 0.3 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, treated with 0.1 N hydrochloric acid for eight hours, aluminum oxide was leached out to the extent of 60% of its content in the residual layer, whereas only 6% ($\alpha = 0.06$) of the silica was leached out.

When the amount of Al_2O_3 added to sodium disilicate was increased to 0.4 mole, the glass underwent intensive breakdown: for all of the components, the amount passing into solution was greatly increased, aluminum ions being

The results of the interaction of the investigated sodium aluminosilicates with 0.1 N hydrochloric acid are given in Table 2 and Fig. 2. The first addition of Al_2O_3 (0.05 mole, i.e., 1.6 mole %) immediately produced a sharp fall in the amount of Na_2O passing into the solution (as compared with the disilicate itself). After an eight-hour treatment of disilicate with 0.1 N hydrochloric acid, $n\text{Na}_2\text{O}$ was 109, whereas the corresponding value for the aluminosilicate $\text{Na}_2\text{O} \cdot 0.05 \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ was 38. The value of α for this aluminosilicate was also less than for the disilicate, although the amount of SiO_2 passing into solution was extremely small in both cases and lagged greatly behind the amount of Na_2O in the solution.

As will be seen from Table 2, the succeeding additions of Al_2O_3 to disilicate in the quantities of 0.15 and 0.3 mole led to still further reductions in the value of $n\text{Na}_2\text{O}$. At the same time, some increase in the values of α and β was observed, which was evidence of the incipient breakdown of the aluminosiliceous skeleton of the glass, from which aluminum ions pass preferentially into the solution (β greater than α). The

TABLE 2

Interaction of Sodium Aluminosilicates with 0.1 N Hydrochloric Acid at 40°

Molecular proportions			Mole sq. cm β α	Time (hours)				
Na ₂ O	Al ₂ O ₃	SiO ₂		1	2	4	6	8
1	0.05	2	$\frac{n}{\beta} \text{Na}_2\text{O}$	12	17	24	32	38
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	—	—	0.01	0.01	0.01
			$\frac{n}{\beta} \text{SiO}_2$	—	—	0.007	0.02	0.02
			β	—	—	0.009	0.006	0.006
			α	—	—	0.0002	0.0003	0.0003
1	0.15	2	$\frac{n}{\beta} \text{Na}_2\text{O}$	0.85	2.5	3.0	4.2	4.9
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	—	—	0.006	0.03	0.02
			$\frac{n}{\beta} \text{SiO}_2$	—	—	0.006	0.008	0.02
			β	—	—	0.013	0.05	0.03
			α	—	—	0.001	0.001	0.002
1	0.3	2	$\frac{n}{\beta} \text{Na}_2\text{O}$	0.6	1.1	1.2	1.6	2.0
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	—	—	0.36	0.34	0.36
			$\frac{n}{\beta} \text{SiO}_2$	—	—	0.15	0.17	0.22
			β	—	—	1.0	0.71	0.60
			α	—	—	0.06	0.05	0.05
1	0.4	2	$\frac{n}{\beta} \text{Na}_2\text{O}$	14	30	58	88	117
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	6.0	13.0	25	35	48
			$\frac{n}{\beta} \text{SiO}_2$	15	31	64	102	109
			β	1.05	1.07	1.06	1.0	1.02
			α	0.55	0.51	0.56	0.58	0.55
1	0.5	2	$\frac{n}{\beta} \text{Na}_2\text{O}$	9	19	42	71	86
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	4.4	8.7	20	32	41
			$\frac{n}{\beta} \text{SiO}_2$	20	31	91	136	176
			β	0.91	0.90	1.0	0.90	0.96
			α	1.06	0.90	1.08	0.95	1.03
1	1	2	$\frac{n}{\beta} \text{Na}_2\text{O}$	5.3	10.4	23.0	34	47
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	4.7	9.7	22.0	34	46
			$\frac{n}{\beta} \text{SiO}_2$	10	20	41.0	66	91
			β	0.90	0.93	0.95	1.0	0.98
			α	0.94	0.96	0.90	0.96	0.97
Vitreous nepheline								
1	1.04	2.17	$\frac{n}{\beta} \text{Na}_2\text{O}$	4.0	8.6	20	35	47
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	4.5	10.2	23	37	49
			$\frac{n}{\beta} \text{SiO}_2$	11	24	45	71	106
			β	1.08	1.1	1.1	1.0	1.0
			α	1.1	1.2	1.04	1.07	1.03
Natural crystalline nepheline								
			$\frac{n}{\beta} \text{Na}_2\text{O}$	27	53	79	74	72
			$\frac{n}{\beta} \text{Al}_2\text{O}_3$	35	66	91	96	96
			$\frac{n}{\beta} \text{SiO}_2$	76.0	140	177	179	149

completely washed out of the layer attacked and SiO₂ being removed to the extent of about 55%. As a result of the action of 0.1 N hydrochloric acid on glass of this composition, a weak spongy residual layer of almost pure silicic acid was formed on the surface. Further increase in the amount of Al₂O₃ added to sodium disilicate resulted in an increase in the amount of SiO₂ passing into the solution from the glass, and the aluminosilicate Na₂O·0.5Al₂O₃·2SiO₂, when treated with hydrochloric acid, behaved in such a way that the proportions of the oxides passing into solution corresponded to the proportions existing in the glass before its treatment with acid:

the glass practically dissolved, and the values of α and β approximated to unity. A similar behavior was found for a glass corresponding in composition to sodium disilicate with the addition of one mole of Al_2O_3 , when treated with 0.1 N hydrochloric acid.

As will be seen from Table 2 and Fig. 2, the values of $n_{\text{Na}_2\text{O}}$ fall as we pass to compositions having an Al_2O_3 addition of more than 0.4 mole. The rate of the breakdown of vitreous nepheline prepared by fusing the natural product is the same as that of the aluminosilicate having the oxide proportions of 1:1:2. Natural crystalline nepheline is broken down by 0.1 N hydrochloric acid appreciably more rapidly than the vitreous form, a fact that is probably to be explained by the greater possibility for the solution to penetrate into the sample owing to the presence of cleavage planes.

TABLE 3

Comparison of the Instabilities of Sodium Silicates and Aluminosilicates in 0.1 N HCl (40°, 8 hours)

Indexes	$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	Moles of SiO_2 added to the disilicate				Moles of Al_2O_3 added to the disilicate					
		0.3	0.6	1.0	2.0	0.05	0.15	0.3	0.4	0.5	1.0
$n_{\text{Na}_2\text{O}} \cdot 10^{-6}$	109	57	28	10	1.7	38	4.9	2.0	117	86	47
$n_{\text{SiO}_2} \cdot 10^{-6}$	0.3	0	0	0	0	0.02	0.02	0.22	109	176	91
$n_{\text{Al}_2\text{O}_3} \cdot 10^{-6}$	—	—	—	—	—	0.01	0.02	0.36	48	41	46
α	0.001	0	0	0	0	0.0003	0.002	0.06	0.55	1.03	0.97
β	—	—	—	—	—	0.006	0.03	0.6	1.02	0.96	0.98
δ	80	46	25	10	2.2	29	3.9	1.6	105	80	53

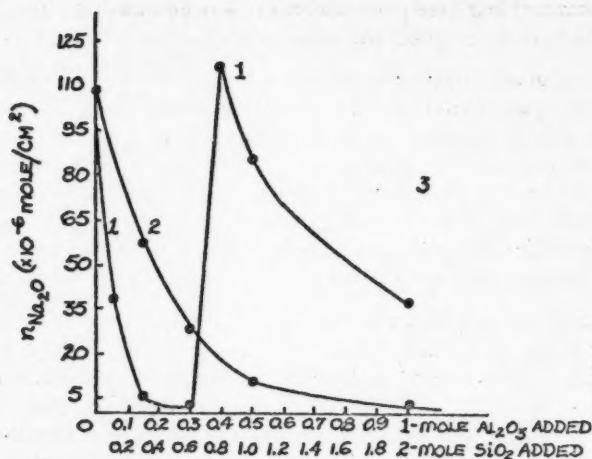


Fig. 3. Comparison of the instabilities of silicates and of the equivalent aluminosilicates in 0.1 N hydrochloric acid; 1) sodium aluminosilicates; 2) sodium silicates; 3) natural nepheline

lent addition of 0.15 mole of Al_2O_3 reduces it by a factor of 20. Further additions of Al_2O_3 increase the depth of the attacked layer up to a certain limit.

On the curve in Fig. 3 that expresses the relation between the amount of Na_2O passing into the solution and the amount of Al_2O_3 added to the disilicate, there is a maximum in the region of the composition $\text{Na}_2\text{O} \cdot 0.4 \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$. This composition, however, does not correspond to any particular point on the phase diagram of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

With increase in the addition of SiO_2 to sodium disilicate, the instability of the resulting silicate falls continuously. The residual siliceous layer on the surface of sodium silicates does not undergo further destruction, and for all of the investigated silicates, apart from the disilicate, the value of α remains equal to zero. In the case of

In Table 3 and Fig. 3 results are given that indicate the comparative stabilities of sodium silicates and the corresponding aluminosilicates to 0.1 N hydrochloric acid. It will be seen that we regard each of the investigated glasses as disilicate having an addition of a certain number of moles of SiO_2 or Al_2O_3 . By the use of such a method of representation, it is possible to make a very precise comparison of the relative effects of the presence of SiO_2 and Al_2O_3 in sodium silicates on their instabilities in aqueous solutions. The value of δ given in Table 3 characterizes the depth of the attacked layer or, what amounts to the same, its thickness; it is calculated by the formula that we cited in a previous paper [8].

The results cited indicate that small additions of Al_2O_3 to sodium disilicate are much more effective in reducing instability than equivalent additions of SiO_2 . Thus, an addition of 0.3 mole of SiO_2 produces a reduction in the depth of the attacked layer of disilicate by a factor of 1.7, whereas the equivalent

aluminosilicates, however, α rises continuously as the aluminum content increases, and for the aluminosilicate having oxide proportions of 1:0.5:2, $\alpha = 1$. This difference in the behavior of additions of Al_2O_3 and SiO_2 with respect to the nature and degree of the breakdown of sodium silicates can be explained from the point of view of redistribution of bonds in the glass resulting from these additions.

DISCUSSION OF RESULTS

In sodium disilicate, on the average three apexes of each silicon-oxygen tetrahedron are bound to neighboring tetrahedra, and only one apex is bound to sodium. When a certain amount of SiO_2 is added to disilicate, silicon-oxygen groups that are attached to one another at all apexes appear. The number of such groups increases with increase in the amount of SiO_2 added, and this increases the stability of the skeleton with respect to the action of acid solutions.

When Al_2O_3 is added to disilicate, then as indicated above there is on the one hand an increase in the number of Si-O-Si linkages owing to the fact that the aluminum-oxygen tetrahedron with its excess negative charge is able to retain a sodium ion in its neighborhood, and, on the other hand, the number of silicon-oxygen groups linked together is greatly reduced, because every aluminum-oxygen tetrahedron can bind four silicon-oxygen groups.

The following types of bonds, which apparently differ energetically among themselves, can be considered to be present in vitreous sodium aluminosilicates: 1) Si-O-Si, all of the apexes of the silicon-oxygen tetrahedra being directly attached to one another; 2) Si-O-Al or Si-O-Na, the remaining three apexes being attached to silicon; 3) Al-O-Si-O-Al or Na-O-Si-O-Al, only two apexes of the silicon oxygen tetrahedron being attached to silicon; 4) silicon-oxygen groups, three apexes being attached to sodium and aluminum, and one apex with silicon; 5) silicon oxygen tetrahedra in which all apexes are attached to sodium and aluminum. It will be clear that O-Al bonds are not equivalent to O-Na bonds, but they are here included conventionally in one group in order to characterize the degree of depolymerization of silica in glass. The weakest bonds with respect to resistance to the action of acid solutions will be those of Types 4 and 5, for when aluminum ions have been selectively washed away they lead to the formation of isolated silicon-oxygen groups in the skeleton of the glass, and these have enhanced solubility.

The way in which the above types of bond are quantitatively combined in vitreous sodium aluminosilicates determines the degree of instability of the latter in aqueous solutions. The instability of sodium aluminosilicates can be characterized by two quantities. The first quantity (δ) is the depth of thickness of the attacked layer and was introduced by Grebenshchikov for the characterization of the chemical stability of glasses [12]; it is a measure of the breakdown of the electrovalent bond O-Na, and has been determined by us, as indicated in a previous paper [8], from the amount of Na_2O passing into solution. The values of α and β characterize the extent to which the skeleton of the glass is broken down, and hence the breakdown also of the residual aluminosiliceous layer formed on the surface of the glass as a result of exchange between sodium and hydrogen ions.

The effect of additions of SiO_2 to sodium disilicate is reflected both in the reduction of the depth of the layer of glass disrupted by the action of acid solutions, and in the stabilization of the silica skeleton. Additions of Al_2O_3 reduce the degree of breakdown of aluminosilicate glasses to a considerably greater extent than the equivalent additions of SiO_2 . At the same time, however, the degree of breakdown in the residual layer is increased. This breakdown proceeds as follows: under the action of acids aluminum ions are preferentially leached from the alumina-silica skeleton, and the surface of the glass becomes enriched in silica. The greater the relative content of Al_2O_3 , in comparison with SiO_2 , in soda-alumina-silica glasses, the greater the extent to which the alumina-silica skeleton is weakened with respect to attack by acids.

As pointed out above, increase in the amount of Al_2O_3 added to sodium disilicate results in increase in the number of sodium ions required to compensate for the negative charges of the aluminum-oxygen tetrahedra. Thus, for an aluminosilicate of composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, all of the sodium ions may be associated with aluminum-oxygen tetrahedra. This type of binding of sodium ions is apparently stronger than the Si-O-Na binding. This is probably the explanation of the slower breakdown of nepheline glass, as compared with that of a glass having an addition of 0.5 mole of Al_2O_3 , although the nature of the breakdown is the same in both cases.

The notable fall in the amount of Na_2O passing into solution observed when small amounts of Al_2O_3 are added to disilicate cannot be explained solely by the attachment of sodium ions to aluminum-oxygen tetrahedra. Here we must probably take into account the stabilizing effect of aluminum ions on the Si-O-Na linkage.

On the basis of all these considerations, we may form the following picture of the processes occurring when sodium aluminosilicates interact with solutions of acids. The primary process, as in the case of sodium silicates, is the exchange of sodium ions attached through oxygen to silicon with hydrogen ions from the solution. Later, exchange occurs also between aluminum and hydrogen ions, and this second reaction apparently occurs more slowly.

Together with the passage of aluminum ions into the solution, transfer must occur also of the sodium ions associated with the aluminum-oxygen tetrahedra. This, in fact, may be the explanation of the sharp increase in the amount of Na_2O passing into solution over a comparatively narrow range of compositions (Fig. 3). When aluminum ions have been washed from the skeleton, isolated silicon-oxygen groups, or small aggregates of these, begin to pass into the solution. The exchange between aluminum ions in the glass and hydrogen ions is apparently more dependent on the hydrogen ion concentration than the exchange between sodium ions and hydrogen ions.

SUMMARY

1. The chemical stability of vitreous sodium aluminosilicates can be characterized by the depth of the attacked layer of glass (δ), which is a measure of the breakdown of electrovalent O-Na bonds, and by the degree of breakdown suffered by the aluminum-silicon-oxygen of the glass, expressed by the proportions of the Al_2O_3 and SiO_2 original'v present in the residual surface layer that have passed into the solution.

2. With increased additions of SiO_2 to sodium silicates, the depth of the attacked layer of glass falls and the silica skeleton is strengthened.

3. When alumina is introduced into sodium silicates, on the one hand there is an increase in the number of silicon-oxygen groups that become united owing to the neutralization by sodium ions of the extra negative charge of the aluminum-oxygen tetrahedra, and on the other hand, owing to the formation of Si-O-Al linkages, depolymerization of silica in the glass increases, with the result that the instability of aluminosilicate glasses in acid solutions increases greatly when the amount of aluminum oxide added to sodium disilicate exceeds 0.3 mole.

4. The mechanism of the interaction of sodium aluminosilicates with solutions of acids may be regarded as the combination of processes of ion exchange between sodium and aluminum in the glass and hydrogen in the solution, followed by the passage into the solution of small isolated aggregates of silicon-oxygen groups.

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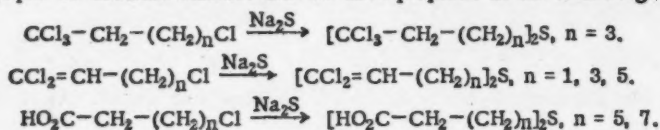
SYNTHESIS OF SULFUR-CONTAINING POLYHALO COMPOUNDS AND OF ω, ω' -THIODICARBOXYLIC ACIDS

A. N. Nesmeyanov, L. I. Zakharkin, and R. G. Petrova

The accessibility of tetrachloroalkanes of structure $\text{CCl}_3-\text{CH}_2-(\text{CH}_2)_n\text{Cl}$ [1] ($n = 1, 3, 5, 7$), and of the trichloroalkenes $\text{CCl}_2=\text{CH}-(\text{CH}_2)_n\text{Cl}$ [2] and ω -chloro carboxylic acids [3] that are readily prepared from them, permits the synthesis of a number of sulfur derivatives containing trichloromethyl, dichlorovinyl, or carboxyl groups. We know only of three very short communications relating to the synthesis of sulfides containing trichloromethyl or dichlorovinyl groups and having more than two carbon atoms in the radical and to the synthesis of ω, ω' -thio dicarboxylic acids having more than four carbons in the radical.

Thus, in a patent [4] reference is made to the preparation of 5,5'-thiodivaleric acid by the hydrolysis of bis(5,5,5-trichloropentyl) sulfide, but neither the reaction conditions nor the proportions of reactants are given, and none of the properties of bis(5,5,5-trichloropentyl) sulfide are described. In another patent [5] there is a description of the preparation of 5,5'-sulfonyldivaleric acid from 1,4-dichlorobutane. A brief indication of the method of preparation of 5,5'-thiodivaleric acid from 5-bromovaleric acid has also appeared [6].

In the present paper we describe sulfides that we have prepared in the following ways:



By the action of sodium sulfide on 1,1,3-trichloropropene, on 1,1,5-trichloro-1-pentene, and on 1,1,7-trichloro-1-heptene we have obtained good yields of bis(3,3-dichloroallyl) sulfide, bis(5,5-dichloro-4-pentenyl) sulfide, and bis(7,7-dichloro-6-heptenyl) sulfide. Reaction was fairly rapid, and was complete in three hours. Similarly, more prolonged heating of 1,1,1,5-tetrachloropentane with sodium sulfide gave bis(5,5,5-trichloropentyl) sulfide in a yield of more than 80%, a small amount of the dehydrochlorinated sulfide being obtained as by-product. In the case of the reaction of 1,1,1,3-tetrachloropropane with sodium sulfide, dehydrochlorination was the main reaction, and it was not found possible to obtain bis(3,3,3-trichloropropyl) sulfide. The chlorine-containing sulfides obtained were quite stable compounds, distillable without decomposition under reduced pressure.

7,7'-Thiodiheptanoic acid and 9,9'-thiodinonanoic acid were obtained in good yield by the action of sodium sulfide on the salts of the corresponding chloro carboxylic acids in aqueous solution. From these acids, the ethyl and butyl esters were prepared in the usual way. The esters of 7,7'-thiodiheptanoic acid are liquids, distillable without decomposition under reduced pressure; the esters of 9,9'-thiodinonanoic acid are low-melting solids.

The sulfides obtained, which contained trichloromethyl, dichlorovinyl, and carboxyl groups, were oxidized to sulfoxides and sulfones. A solution of hydrogen peroxide in glacial acetic acid was used as oxidizing agent. Bis(5,5,5-trichloropentyl) sulfoxide is a crystalline solid, and the sulfoxides containing dichlorovinyl groups are thick oils, which do not crystallize after long standing. Some of the sulfones that we have prepared are substances that readily crystallize and have sharp melting points.

When bis(3,3-dichloroallyl) sulfone is treated with chlorine in chloroform solution, with irradiation and application of heat, two atoms of chlorine are taken up, and a crystalline product of m.p. 187-188° is obtained; it was not investigated in detail.

EXPERIMENTAL

Bis(3,3-dichloroallyl) Sulfide $[\text{CCl}_2=\text{CH}-\text{CH}_2]_2\text{S}$

A mixture of 40 g of 1,1,3-trichloropropene, an aqueous solution of 34 g of sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), and 100 ml of ethanol was boiled under stirring for three hours. The alcohol was distilled off, and the residue was poured into water and extracted with chloroform. The chloroform was distilled off, and the residue was vacuum-distilled,

yielding 27.8 g (80%) of bis(3,3-dichloroallyl) sulfide, b.p. 92-94° at 1 mm, n_D^{20} 1.5630; d_4^{20} 1.4451; found MR 56.55; calculated MR 56.44.

Found %: C 28.67; 28.58; H 2.39; 2.50
 $C_6H_6Cl_4S$. Calculated %: C 28.57; H 2.37

Oxidation of bis(3,3-dichloroallyl) sulfide with a solution of 30% hydrogen peroxide in glacial acetic acid yielded bis(3,3-dichloroallyl) sulfone, m.p. 114-115° (from alcohol).

Found %: C 25.60; 25.54; H 2.11; 1.91
 $C_6H_6Cl_4O_2S$. Calculated %: C 25.35; H 2.11

Addition of Chlorine to Bis(3,3-dichloroallyl) Sulfone

A solution of 5 g of the sulfone in 30 ml of chloroform was illuminated and heated, and chlorine was passed for two hours. The chloroform was then distilled off, and the residue was recrystallized from a large amount of ethanol, yielding 2.7 g of substance, m.p. 187-188°.

Found %: C 20.46; 20.53; H 1.99; 1.78
 $C_8H_6Cl_6O_2S$. Calculated %: C 20.31; H 1.72

Bis(5,5-dichloro-4-pentenyl) Sulfide [$CCl_2=CH-(CH_2)_3$] $_2S$

From 40 g of 1,1,5-trichloro-1-pentene, 28 g of sodium sulfide, 12 ml of water, and 80 ml of ethanol, the procedure described above yielded 27 g (75%) of bis(5,5-dichloro-4-pentenyl)sulfide, b.p. 147° (1 mm); n_D^{20} 1.5368; d_4^{20} 1.2818; found MR 74.92; calculated MR 74.91.

Found %: C 39.31; 39.34; H 4.57; 4.64
 $C_{18}H_{14}Cl_4S$. Calculated %: C 38.96; H 4.54

Oxidation of bis(5,5-dichloro-4-pentenyl) sulfide with a solution of 30% hydrogen peroxide in glacial acetic acid yielded the sulfone, which was an oil that could not be vacuum-distilled without decomposition.

Bis(7,7-dichloro-6-heptenyl) Sulfide [$CCl_2=CH-(CH_2)_5$] $_2S$

From 20 g of 1,1,7-trichloro-1-heptene, 12 g of sodium sulfide ($Na_2S \cdot 9H_2O$) in 10 ml of water, and 60 ml of ethanol, the procedure described above yielded 14.1 g (78%) of bis(7,7-dichloro-6-heptenyl) sulfide, b.p. 186-187° (1.5 mm); n_D^{20} 1.5214; d_4^{20} 1.1853; found MR 93.57; calculated MR 93.39.

Found %: C 45.96; 46.27; H 6.22; 6.09
 $C_{14}H_{22}Cl_2S$. Calculated %: C 46.15; H 6.04

Oxidation of bis(7,7-dichloro-6-heptenyl) sulfide with a solution of 30% hydrogen peroxide in glacial acetic acid yielded the sulfone as an oil that could not be vacuum-distilled without decomposition.

Bis(5,5,5-trichloropentyl) Sulfide [$CCl_3-CH_2-(CH_2)_3$] $_2S$

A vigorously stirred mixture of 105 g of 1,1,1,5-tetrachloropentane, a solution of 60 g of sodium sulfide ($Na_2S \cdot 9H_2O$) in 30 ml of water, and 150 ml of ethanol was boiled for eight hours. The alcohol was distilled off, and the residue was poured into water and extracted with chloroform. The chloroform extract was dried with calcium chloride, the chloroform was distilled off, and the residue was vacuum-distilled, yielding 82.5 g of a fraction boiling at 203-205° at 5 mm. This substance crystallized out almost completely when cooled. A small amount of oil was removed by filtration, and the crystals were washed several times with methanol; m.p. 35-36° (from alcohol).

Found %: C 31.64; 31.68; H 4.29; 4.36; S 8.30; 8.33
 $C_{18}H_{15}Cl_3S$. Calculated %: C 31.49; H 4.19; S 8.38

Analysis of the noncrystallizing oil showed that it consisted of a mixture of partially dehydrochlorinated products, which gave 5,5'-thiodivaleric acid when hydrolyzed with concentrated sulfuric acid.

Oxidation of 10 g of bis(5,5,5-trichloropentyl) sulfide with 3.3 g of 27% hydrogen peroxide in 25 ml of glacial acetic acid yielded bis(5,5,5-trichloropentyl) sulfoxide, m.p. 67-68° (from petroleum ether).

Found %: C 30.63; 30.81; H 4.04; 4.28; S 7.92; 7.84
 $C_{18}H_{15}Cl_3OS$. Calculated %: C 30.23; H 4.03; S 8.06

Oxidation of bis(5,5,5-trichloropentyl) sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid yielded bis(5,5,5-trichloropentyl) sulfone, m.p. 114-115° (from alcohol).

Found %: C 29.40; 29.39; H 4.10; 4.02; S 7.59; 7.51
 $C_{13}H_{15}Cl_2O_2S$. Calculated %: C 29.05; H 3.87; S 7.74

7,7'-Thiodiheptanoic Acid [$CO_2H-(CH_2)_5$] $_2S$

The sodium salt of 7-chloroheptanoic acid was prepared from 34 g of 7-chloroheptanoic acid and 8 g of caustic soda in 100 ml of water, and to the solution obtained 25 g of sodium sulfide ($Na_2S \cdot 9H_2O$) was added. The mixture was heated under reflux for two hours. The cooled solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The white precipitate of 7,7'-thiodiheptanoic acid was filtered off, washed with cold water, and dried. The yield was 26.8 g (89.5%); m.p. 96-97° (from dilute alcohol).

Found %: C 58.23; 57.93; H 8.87; 9.12; S 10.62; 10.57
 $C_{14}H_{26}O_4S$. Calculated %: C 57.95; H 9.00; S 11.03

The sulfone was prepared by oxidation of the sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid; m.p. 156-157° (from alcohol).

Found %: C 52.26; 52.22; H 8.07; 8.18
 $C_{14}H_{26}O_6S$. Calculated %: C 52.17; H 8.07

The diethyl ester of 7,7'-thiodiheptanoic acid had the following constants: b.p. 183-184° (1.5 mm); n_D^{20} 1.4660; d_4^{20} 0.9951; found MR 96.64; calculated MR 96.48.

Found %: C 62.65; 62.53; H 9.57; 9.64; S 9.38
 $C_{18}H_{34}O_4S$. Calculated %: C 62.42; H 9.82; S 9.22

The dibutyl ester of 7,7'-thiodiheptanoic acid had the following constants: b.p. 214-215° (1.5 mm); n_D^{20} 1.4641; d_4^{20} 0.9678; found MR 114.91; calculated MR 115.11.

Found %: C 65.67; 65.61; H 9.89; 9.87; S 8.18; 8.06
 $C_{22}H_{42}O_4S$. Calculated %: C 65.67; H 10.44; S 7.97

9,9'-Thiodinonanoic Acid [$CO_2H-(CH_2)_7$] $_2S$

A solution of the sodium salt of 9-chlorononanoic acid prepared from 27 g of 9-chlorononanoic acid and 5.7 g of caustic soda in 100 ml of water was heated with 17 g of sodium sulfide for three hours, and yielded 22.4 g (92%) of 9,9'-thiodinonanoic acid, m.p. 98-99° (from alcohol).

Found %: C 62.40; 62.58; H 10.28; 10.05; S 9.50; 9.24
 $C_{18}H_{34}O_4S$. Calculated %: C 62.42; H 9.82; S 9.22

The sulfonyldinonanoic acid was obtained by oxidation of the sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid; m.p. 148-149° (from alcohol).

Found %: C 56.83; 56.74; H 9.03; 9.03; S 8.67; 8.56
 $C_{18}H_{34}O_6S$. Calculated %: C 57.12; H 9.00; S 8.46

The diethyl ester of 9,9'-thiodinonanoic acid had b.p. 219-220° (2 mm); m.p. 37-38° (from petroleum ether).

Found %: C 66.19; 65.91; H 10.46; 10.47
 $C_{22}H_{42}O_4S$. Calculated %: C 65.65; H 10.44

The dibutyl ester of 9,9'-thiodinonanoic acid had b.p. 239-241° (1.5 mm); m.p. 22-23° (from petroleum ether); n_D^{20} 1.4660.

Found %: C 68.11; 68.29; H 11.11; 11.10
 $C_{26}H_{50}O_4S$. Calculated %: C 68.15; H 10.91

SUMMARY

1. The following compounds, not previously described, have been prepared by the action of sodium sulfide on polychloro derivatives of formula $CCl_2=CH(CH_2)_nCl$ and $CCl_3-CH_2-(CH_2)_nCl$: bis(3,3-dichloroallyl) sulfide, bis(5,5-dichloro-4-pentenyl) sulfide, bis(7,7-dichloro-6-heptenyl) sulfide, and bis(5,5,5-trichloropentyl) sulfide.

2. 7,7'-Thiodiheptanoic and 9,9'-thiodinonanoic acids, which have not been described previously, have been prepared by the action of sodium sulfide on the corresponding ω -chloro carboxylic acids. Their diethyl and dibutyl esters have been prepared.

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• See Consultants Bureau Translation, page 879.

SOME REACTIONS OF 3,3,3- AND 1,1,3-TRICHLOROPROPENES

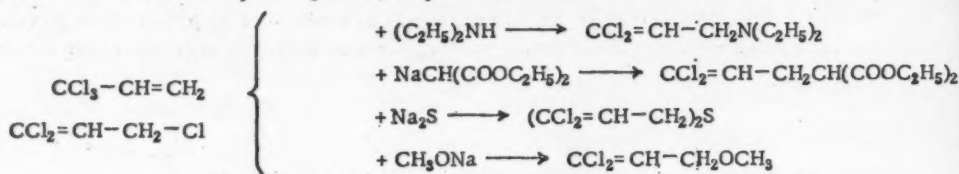
A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost, and R. Kh. Freidlina

Until recently 1,1,2-trichloropropene has been erroneously assigned the structure of 3,3,3-trichloropropene [1] and this has led to incorrect inferences concerning the reactivity of 3,3,3-trichloropropene. It has been stated that 3,3,3-trichloropropene appears to be unable to undergo the allyl rearrangement [2], to exchange the chlorines of its trichloromethyl group for fluorines [3], and to add hydrogen chloride and hydrogen bromide [4].

Two of the authors of the present paper together with Firstov [5] were the first to synthesize 3,3,3-trichloropropene from 1,1,1,3-tetrachloropropane, and they showed that it would undergo the allyl rearrangement, unite with chlorine and bromine, polymerize in presence of benzoyl peroxide, and condense with benzene in presence of aluminum chloride (in this reaction allyl rearrangement occurred). It was later shown that 3,3,3-trichloropropene combines, in presence of benzoyl peroxide, with bromotrichloromethane and with hydrogen bromide. In the course of this work we discovered a rearrangement involving the transfer of a chlorine atom in the intermediately formed radical [6].

1,1,3-Trichloropropene was first prepared in 1948 [7], but its reactions have received only a little study [5, 7]. In the present paper we describe the results of the reactions of certain nucleophilic and other reagents on 3,3,3-trichloropropene and 1,1,3-trichloropropene.

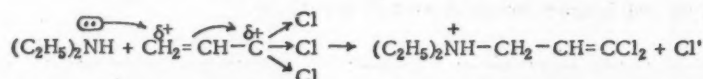
As nucleophilic reagents we have used diethylamine, sodiummalonic ester, sodium sulfide, and sodium methoxide. In the case of reaction with 1,1,3-trichloropropene replacement of the allyl chlorine by the nucleophilic residue of the reagent was observed. The reactions of 3,3,3-trichloropropene with nucleophilic reagents were always accompanied by allyl rearrangement, leading to the same compounds as those formed by the action of the same reagents on 1,1,3-trichloropropene. These reactions may be represented by the schemes:



The identity of the dichloro(diethylamino)propenes obtained from the two trichloropropenes by the action of diethylamine was shown by a mixture melting point test on their hydrochlorides.

The identity of the products obtained by the action of sodiummalonic ester on the two trichloropropenes, and their structure, were shown by conversion into glutaric acid by hydrolysis and decarboxylation. The identity of the bis(dichloropropenyl) sulfides obtained from the two trichloropropenes was established by a mixture melting point test on the sulfones prepared from these sulfides. By the action of sodium methoxide on 3,3,3-trichloropropene and on 1,1,3-trichloropropene, the same compound was obtained in each case, and it evidently had the structure 1,1-dichloro-3-methoxypropene; when it was treated with chlorine under very mild conditions, a pentachloro compound was formed which probably had the structure $\text{CCl}_3-\text{CHClCHClOCH}_3$.

It must be emphasized that the reactions of nucleophilic reagents with 3,3,3-trichloropropene proceed with good yield under conditions that preclude preliminary isomerization into 1,1,3-trichloropropene. It may be supposed that the center for nucleophilic attack in 3,3,3-trichloropropene is the methylene group, since the carbon of the trichloromethyl group is powerfully shielded by means of chlorine atoms. Hence, the reactions of 3,3,3-trichloropropene studied here belong to the type that occur with transfer of reaction center [8]. The reaction of 3,3,3-trichloropropene with diethylamine may be represented by the scheme:



It is of interest to note that in the case of 3,3-dichloropropene reaction with nucleophilic reagents proceeds simultaneously in two directions: with and without isomerization [9]. This is evidently a consequence of the greater

accessibility of the carbon of the dichloromethyl group to nucleophilic attack. 3,3,3-Trichloro-2-methylpropene reacts with nucleophilic reagents with isomerization [10].

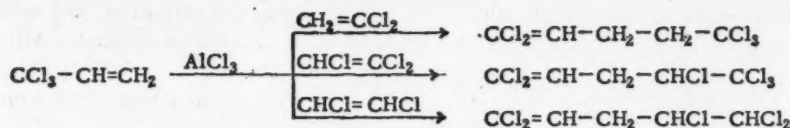
Also, a study has been made of the action of organomagnesium compounds on the isomeric trichloropropenes. In the reaction of butylmagnesium bromide both with 3,3,3-trichloropropene and with 1,1,3-trichloropropene, the main product was 1,1-dichloro-1-heptene, the structure of which was proved by hydrolysis to heptanoic acid. When the reaction was carried out with phenylmagnesium bromide, not only was 1,1-dichloro-3-phenylpropene obtained, but also biphenyl. It should be noted that these reactions, as is usual in reactions of a homolytic nature, proceed with formation of a number of other products, which were not investigated further.

When cuprous cyanide reacted with 3,3,3-trichloropropene and with 1,1,3-trichloropropene, the same product, 4,4-dichloro-3-butenenitrile, was obtained in each case in good yield. The identity of the two products was proved by preparation of the crystalline tetrachloride obtained by addition of chlorine, and also by a mixture melting point. The structure of the unsaturated nitrile was proved to be 4,4-dichloro-3-butenenitrile by hydrolysis of succinic acid. The crystalline tetrachloride had the structure 3,4,4,4-tetrachlorobutyronitrile, which was confirmed by the formation of 4,4,4-trichlorocrotononitrile by dehydrochlorination with alcoholic alkali.

By the action of Raney nickel on 3,3,3-trichloropropene in an ethanol medium, a tetrachlorohexadiene was obtained which apparently had the structure $(\text{CCl}_2=\text{CH}-\text{CH}_2-)_2$, since on hydrolysis in presence of concentrated sulfuric acid it yielded adipic acid, although in low yield.

Hence, also in reactions that are probably homolytic in nature, 1,1,3-trichloropropene reacts at the allyl chlorine and 3,3,3-trichloropropene reacts with allyl rearrangement.

The high reactivity of the trichloropropenes studied makes it possible to apply them to the synthesis of higher polychloroalkanes. Thus, 3,3,3-trichloropropene unites with polyhaloethylenes in presence of AlCl_3 :



The structure of the product of the first reaction was established by hydrolysis to glutaric acid. The structures of the products of the other two reactions are suggested by analogy. It is interesting that, although 1,1,3-trichloropropene undergoes this reaction, the yields of the products are considerably less.

EXPERIMENTAL

Action of Diethylamine on 3,3,3-Trichloropropene

A solution of 10 g (0.055 mole) of 3,3,3-trichloropropene and 10 g (0.137 mole) of diethylamine in methanol was heated under reflux for eight hours. The alcohol was distilled off from a water bath, and the residue was dissolved in dilute hydrochloric acid and extracted with ether to remove neutral products. The hydrochloric acid solution was made alkaline in the cold with caustic soda solution, and the oil that separated was extracted with ether. The ether extract was dried with sodium sulfate. Vacuum distillation yielded 9.3 g (74%) of 3,3-dichloro-N,N-diethylallylamine, b.p. 65-66° (7 mm); n_D^{20} 1.4708; d_4^{20} 1.0693; found MR 47.56; calculated MR 47.73. A crystalline deposit formed in the substance after it had stood for a short time. The melting point of the hydrochloride of 3,3-dichloro-N,N-diethylallylamine was 139-140° (from alcohol + ether).

	Found %: Cl 48.80; 48.80
$\text{C}_7\text{H}_{14}\text{Cl}_2\text{N}$	Calculated %: Cl 48.74

Action of Diethylamine on 1,1,3-Trichloropropene

A solution of 10 g (0.055 mole) of 1,1,3-trichloropropene and 11 g (0.150 mole) of diethylamine in methanol was heated for three hours. The reaction mixture was treated as above, and yielded 8.1 g (65%) of 3,3-dichloro-N,N-diethylallylamine, b.p. 65-66° (7 mm); n_D^{20} 1.4716; d_4^{20} 1.0694. Hydrochloride m.p. 139-140°. A mixture melting point test on the two hydrochlorides showed no depression.

Action of Sodiomalonic Ester on 1,1,3-Trichloropropene

1,1,3-Trichloropropene (30 g, i.e., 0.16 mole) was added under cooling (evolution of heat was observed) to sodiomalonic ester prepared from 3.2 g (0.20 mole) of malonic ester and 4.6 g of sodium in 70 ml of absolute ethanol. The reaction mixture was heated for three hours under reflux and cooled. Water was added until the

sodium chloride had dissolved, and the oil that separated was extracted with carbon tetrachloride, the extract being dried with magnesium sulfate. Vacuum distillation yielded 23.5 g (50%) of 3,3-dichloroallylmalonic ester, b.p. 102-103° at 1.5 mm, and 11.2 g of bis(3,3-dichloroallyl)malonic ester, b.p. 138-140° at 1.5 mm. 3,3-Dichloroallylmalonic ester had the following constants: n_D^{20} 1.4633; d_4^{20} 1.2135; found MR 61.09; calculated MR 60.95.

$C_{10}H_{14}Cl_2O_4$ Found %: C 44.49; 44.66; H 5.28; 5.33
 Calculated %: C 44.62; H 5.24

The structure of 3,3-dichloroallylmalonic ester was proved by its hydrolysis with sulfuric acid to glutaric acid.

Bis(3,3-dichloroallyl)malonic ester melted at 39-40° (from petroleum ether).

$C_{13}H_{16}Cl_4O_4$ Found %: C 41.56; 41.83; H 4.29; 4.30
 Calculated %: C 41.30; H 4.26

Action of Sodiomalonic Ester on 3,3,3-Trichloropropene

A mixture of sodiomalonic ester, prepared from 24 g of malonic ester and 3.5 g of sodium in 50 ml of absolute ethanol, and 21 g of 3,3,3-trichloropropene was heated under reflux for five hours. Fractionation of the reaction products yielded 16.3 g of 3,3-dichloroallylmalonic ester (n_D^{20} 1.4635; d_4^{20} 1.2135) and 10.6 g of bis(3,3-dichloroallyl)malonic ester, m.p. 39-40°, which gave no melting-point depression in a mixture test with the analogous product from the preceding experiment. When the dichloroallylmalonic ester was hydrolyzed with sulfuric acid, glutaric acid was again obtained.

Action of Sodium Sulfide on 3,3,3-Trichloropropene

A stirred mixture of 15 g of 3,3,3-trichloropropene with a solution of 12 g of $Na_2S \cdot 9H_2O$ in 70 ml of ethanol and 10 ml of water was heated for four hours. The alcohol was then removed (water bath), water was added to the residue, and the oil present was extracted with chloroform. Vacuum distillation yielded 10.1 g (62%) of bis(3,3-dichloroallyl) sulfide, b.p. 101-102° (2 mm); n_D^{20} 1.5628; d_4^{20} 1.4450.

Oxidation of the sulfide with excess of a solution of 30% hydrogen peroxide in glacial acetic acid yielded a sulfone, m.p. 113-114°; it gave no melting-point depression in a mixture test with bis(3,3-dichloroallyl) sulfone, prepared as described previously [11].

Action of Sodium Methoxide on 3,3,3-Trichloropropene

A mixture of 15 g (0.1 mole) of 3,3,3-trichloropropene and a solution of sodium methoxide prepared from 3 g of sodium and 50 ml of methanol was heated in a water bath for three hours. The reaction mixture was diluted with water, and the oil that separated was extracted with ether. The ether extract was washed with water and dried over calcium chloride. The material remaining after removal of ether was fractionated, and yielded 5 g of unchanged 3,3,3-trichloropropene and 7 g (50%) of a substance having b.p. 132-133°; n_D^{20} 1.4558; d_4^{20} 1.2117; found MR 31.62; calculated for $C_4H_5OCl_2$ MR 31.58.

$C_4H_5OCl_2$ Found %: C 34.27; 34.40; H 4.30; 4.41
 Calculated %: C 34.07; H 4.29

Action of Sodium Methoxide on 1,1,3-Trichloropropene

To a sodium methoxide solution prepared by dissolving 3 g (0.18 mole) of sodium in 50 ml of methanol, 15 g (0.1 mole) of $CCl_2=CHCH_2Cl$ was added, a little at a time. Addition of the latter was accompanied by immediate precipitation of sodium chloride. The mixture was heated at the boil for one hour. The product was distilled from a Favorsky flask having a 50 cm fractionating column, and a fraction of b.p. 131-132° was collected (n_D^{20} 1.4558; d_4^{20} 1.2112). The methoxy compound so obtained was treated with chlorine at 60° in the dark. Not only addition, but also substitution occurred (evolution of HCl). Distillation of the chlorination product yielded 15 g of a substance having b.p. 97-98° (5.5 mm); n_D^{20} 1.5098; d_4^{20} 1.5749; found MR 46.77; calculated for $C_4H_5Cl_5O$ MR 46.65.

$C_4H_5Cl_5O$ Found %: Cl 72.90; 72.94
 Calculated %: Cl 71.96.

The yield of the pentachlorocompound was 61% on the amount of trichloropropene taken.

Action of Cuprous Cyanide on 3,3,3-Trichloropropene

A stirred mixture of 50 g (0.34 mole) of 3,3,3-trichloropropene and 32 g (0.18 mole) of cuprous cyanide was heated in an oil bath under reflux, at first at 130°, and then at 160°. Heating was continued until liquid ceased to

drop back from the condenser. The product was distilled from the reaction mixture at 10 mm. A second distillation yielded 30 g (63.8%) of 4,4-dichloro-3-butenenitrile, b.p. 77-78° (11 mm); n_D^{20} 1.4831; d_4^{20} 1.3142; found MR 29.60; calculated for $C_4H_3Cl_2N$ MR 29.76.

	Found %:	C 35.52; 35.69;	H 2.38; 2.49;	Cl 51.75; 51.78
$C_4H_3Cl_2N$.	Calculated %:	C 35.32;	H 2.22;	Cl 52.14

Action of Cuprous Cyanide on 1,1,3-Trichloropropene

The reaction of 1,1,3-trichloropropene with cuprous cyanide proceeds in a similar manner: 15 g of 1,1,3-trichloropropene and 9 g of cuprous cyanide yielded 7.7 g of 4,4-dichloro-3-butenenitrile, b.p. 77-78° (11 mm); n_D^{20} 1.4831; d_4^{20} 1.3122. When they combine with chlorine, both the nitrile obtained from 3,3,3-trichloropropene and that from 1,1,3-trichloropropene yield the same tetrachlorobutyronitrile (see below), m.p. 44° (no depression in mixture test). In the reaction of 1,1,3-trichloropropene with potassium cyanide in an aqueous-alcoholic medium, only a very small yield of 4,4-dichloro-3-butenenitrile was obtained, a fact that may be associated with the instability of this nitrile in an alkaline medium.

Hydrolysis of $CCl_2=CH-CH_2CN$

A mixture of 2 g of the nitrile obtained in the preceding experiments and 10 ml of 90% sulfuric acid was heated at 100-120° until hydrogen chloride ceased to be evolved. The product was poured into water (100 ml). The aqueous solution was extracted with ether (fifteen 20 ml portions), and the ether extracts were dried over calcium chloride. The ether was removed, and the crystalline residue was recrystallized from water and washed with ether on the filter. The product was 0.7 g of succinic acid, m.p. 184-184.5°. In admixture with authentic succinic acid, it melted at 184-185°.

Addition of Chlorine to $CCl_2=CH-CH_2CN$

Through a solution of 33 g (0.24 mole) of $CCl_2=CH-CH_2CN$ in 70 ml of carbon tetrachloride, heated at the boil and illuminated with a 150-watt lamp, chlorine was passed to saturation. The solvent was distilled off, and the crystalline residue was vacuum-distilled. Practically the whole of the product came over at 105-107° at 6.5 mm. It melted, after recrystallization from petroleum ether, at 43.5-44°. The yield was 47.2 g (94%).

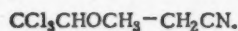
	Found %:	C 23.48; 23.43;	H 1.58; 1.54
$C_4H_3Cl_4N$.	Calculated %:	C 23.22;	H 1.46

Dehydrochlorination of $CCl_3CHCl-CH_2CN$

A solution of 5 g (0.089 mole) of KOH in 50 ml of methanol was added dropwise to an ice-cooled stirred mixture of 19 g (0.091 mole) of 3,4,4,4-tetrachlorobutyronitrile, prepared as described in the previous experiment, and 25 ml of the methanol. The mixture was set aside at room temperature overnight. The product was precipitated with water, separated, washed with water, dried with calcium chloride, and vacuum-distilled. The fraction boiling at 68-73° at 7 mm was collected. The yield of 4,4,4-trichlorocrotononitrile was 12.5 g (82%). In a second distillation almost the whole of the substance came over at 68-69° at 7 mm; n_D^{20} 1.5082; d_4^{20} 1.4237; found MR 35.70; calculated for $C_4H_2O_3N$ MR 34.62 (the literature [12] gives: n_D^{20} 1.5083, d_4^{20} 1.420).

	Found %:	Cl 62.42; 62.28
$C_4H_2Cl_3N$.	Calculated %:	Cl 62.41

When the reaction is carried out with an excess of alkali at a higher temperature, a molecule of alcohol adds to the trichlorocrotononitrile formed. For example, 44 g of the tetrachlorobutyronitrile treated with a solution of 15 g of KOH in 150 ml of methanol at room temperature yielded 28 g of a substance of b.p. 99.5° (6.5 mm); n_D^{20} 1.4820; d_4^{20} 1.3879; found MR 41.59; calculated for $C_5H_5Cl_3NO$ MR 41.35. The structure proposed for this compound is as follows:



	Found %:	C 29.67; 29.78;	H 3.12; 3.23
$C_5H_5Cl_3NO$.	Calculated %:	C 29.65;	H 2.99

Action of Butylmagnesium Bromide on 3,3,3-Trichloropropene

An ethereal solution of butylmagnesium bromide, prepared from 17 g of butyl bromide and 3.7 g of magnesium in 50 ml of ether, was added slowly to a stirred cooled solution of 21 g of 3,3,3-trichloropropene. A precipitate of magnesium salts was formed. When addition of butylmagnesium bromide was complete, the reaction mixture

was heated for ten minutes, and was then cooled and poured into cold water. The ether solution was separated and dried with calcium chloride. Distillation yielded 12.8 g (68%) of 1,1-dichloro-1-heptene, b.p. 59-60° at 9 mm, and 4 g of a fraction boiling over the range 60-170° at 9 mm. The constants of 1,1-dichloro-1-heptene were n_D^{20} 1.4585; d_4^{20} 1.0427; found MR 43.76; calculated MR 43.79. Hydrolysis with sulfuric acid yielded heptanoic acid, from which the anilide, m.p. 64-65°, was prepared. In admixture with an authentic sample it melted at 64-65°.

Action of Butylmagnesium Bromide on 1,1,3-Trichloropropene

To an ethereal solution of butylmagnesium bromide, prepared from 17 g of butyl bromide and 3.7 g of magnesium in 50 ml of ether, 21 g of 1,1,3-trichloropropene was added. Heat was evolved, and the ether came to the boil. After 20-25 minutes, a precipitate of magnesium salts began to appear. The solution was heated in a water bath for two hours. Distillation of the reaction products yielded 6 g (31%) of 1,1-dichloro-1-heptene, b.p. 60-61° at 9 mm, and a large amount of a fraction boiling over the range 60-200° at 9 mm.

Action of Raney Nickel on 3,3,3-Trichloropropene

3,3,3-Trichloropropene (10 g) was gradually added to 6 g of Raney nickel in 20 ml of ethanol. Much heat was evolved, and it was necessary to provide cooling, so that the alcohol did not boil. The reaction mixture was then boiled for 20 minutes. The mixture was cooled, the nickel was removed, water was added to the alcoholic solution, and the oil that separated was extracted with chloroform. The chloroform solution was dried with calcium chloride. Vacuum distillation yielded 3.8 g (48%) of a tetrachlorohexadiene, b.p. 98-100° (8 mm); n_D^{20} 1.5149; d_4^{20} 1.3628; found MR 48.64; calculated MR 48.44.

	Found %:	C 32.90; 32.94;	H 2.98; 2.92
$C_6H_6Cl_4$	Calculated %:	C 32.72;	H 2.72

When the tetrachlorohexadiene was hydrolyzed with sulfuric acid, adipic acid was obtained in low yield.

Addition of 3,3,3-Trichloropropene to 1,1-Dichloroethylene

3,3,3-Trichloropropene (15 g) was added gradually to a stirred mixture of 20 g of 1,1-dichloroethylene and 1 g of aluminum chloride at 15-20°. When addition was complete, the solution was stirred for a further 15 minutes and was then poured into water. The oil obtained was dried with calcium chloride. Vacuum distillation yielded 18.8 g (76%) of 1,1,5,5,5-pentachloro-1-pentene, b.p. 101-104° (12 mm); n_D^{20} 1.5125; d_4^{20} 1.4707; found MR 49.40; calculated MR 59.16.

	Found %:	C 24.42; 24.38;	H 1.87; 1.94
$C_5H_5Cl_5$	Calculated %:	C 24.73;	H 2.06

By hydrolysis of the pentachloropentene with sulfuric acid, glutaric acid was obtained. In a similar way 3,3,3-trichloropropene and trichloroethylene yielded 1,1,4,5,5,5-hexachloro-1-pentene, b.p. 119-120° (10 mm); n_D^{20} 1.5291; d_4^{20} 1.5817; found MR 53.98; calculated MR 54.02.

	Found %:	C 21.45; 21.48;	H 1.50; 1.68
$C_5H_4Cl_6$	Calculated %:	C 21.66;	H 1.44

From 1,2-dichloroethylene, 1,1,4,5,5-pentachloro-1-pentene was prepared; b.p. 105-107° (7 mm); n_D^{20} 1.5225; d_4^{20} 1.5077; found MR 48.89; calculated MR 49.16.

	Found %:	C 24.44; 24.40;	H 1.85; 1.92
$C_5H_5Cl_5$	Calculated %:	C 24.73;	H 2.06

SUMMARY

1. A study has been made of the action of diethylamine, sodiomalonic ester, sodium sulfide, and sodium methoxide on 3,3,3-trichloropropene and 1,1,3-trichloropropene. It has been shown that in all cases, the reaction with 3,3,3-trichloropropene is accompanied by allyl rearrangement, so that the products are the same as those obtained by the action of the same reagents on 1,1,3-trichloropropene.
2. A study has been made of the action of organomagnesium compounds on 3,3,3- and 1,1,3-trichloropropenes. It has been shown that the alkylation of 3,3,3-trichloropropene is accompanied by allyl rearrangement.
3. A study has been made of the action of cuprous cyanide on 3,3,3- and 1,1,3-trichloropropenes, and it has been shown that in the case of 3,3,3-trichloropropene this reaction is accompanied by allyl rearrangement.

4. It has been found that in presence of $AlCl_3$ polyhaloethylenes unite with both 3,3,3-trichloropropene and 1,1,3-trichloropropene.

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• See Consultants Bureau Translation, page 205.

DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 2. TWO GASOLINES FROM KAZANBULAK PETROLEUMS

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This paper • describes the results of a study of the individual hydrocarbon composition of two gasolines from Kazanbulak (Azerbaijani SSR) petroleum. The investigation was carried out by the previously described combination method [1]. This method, which was developed in the Zelinsky Institute of Organic Chemistry and the Lebedev Institute of Physics, is based on the principle of the gradual simplification of the composition of a mixture of hydrocarbons derived from these gasolines, so that it is finally possible to investigate them by the Raman-spectrum method. The obtaining of fractions containing hydrocarbons that are as homogeneous as possible with respect to the types of groups present and to molecular weight is achieved by the successive application at various stages of the investigation of exact rectification, chromatographic separation of aromatic hydrocarbons, and catalytic dehydrogenation of six-membered naphthenes with a view to their conversion into aromatic hydrocarbons and the subsequent separation of these.

We must make some reservations associated with the fact that the work described in this paper was carried out in 1948, when the combination method had not yet been worked out in all details. It was, in fact, on the basis of the experience gained during this investigation that the combination method began to take shape: the accuracy and completeness of analysis attained in this work has been considerably improved upon in later investigations, and in the investigation described in this paper the losses at all stages were appreciably higher than in subsequent investigations. We must also point out that the dehydrogenation catalyst used was of low activity. Also, at the time when this work was carried out we had not yet at our disposal many of the hydrocarbon standards that are so important for the complete quantitative, or even qualitative, analysis of gasolines with the aid of Raman spectra. Owing to these circumstances, the analysis of the gasolines discussed below is far from complete.

In spite of the incompleteness of the analysis, we consider that it is desirable to publish the results obtained, since in our opinion they are of definite interest even in such a form: actually, although the two Kazanbulak gasolines were obtained from petroleum having the same place of origin (at different horizons), they were found to differ greatly from one another in individual composition. Also, one of the gasolines differed considerably in composition from the other gasolines that we have investigated by this method. Hence, the analytical results for these gasolines, in spite of the deficiencies pointed out above, enable us to extend our knowledge concerning the individual composition of Soviet gasolines.

The Kazanbulak petroleum that we studied were obtained directly from their source of origin. The scheme of investigation was completely identical with that given in the communication cited above [1], and the same letters are used to denote the fractions. The gasolines investigated will be denoted by TsK-1 and TsK-2.

As a result of our investigations more than 70 individual hydrocarbons were found in the two gasolines.

The numbers of hydrocarbons found and their distribution among the classes are given in Table 1. In Table 2 we give a list of the individual hydrocarbons found in Kazanbulak gasolines and their percent contents. It will be seen that 25 hydrocarbons have been determined quantitatively in the gasoline TsK-2, and this gasoline (which distilled over at temperatures ranging to 150°) was accounted for quantitatively to the extent of 55%. In the gasoline TsK-1, 33 hydrocarbons were determined quantitatively, but, owing to its more complex composition, only 40% of the whole gasoline (which distilled over at temperatures ranging to 150°) was accounted for quantitatively. Improvement in procedure and increase in the number of hydrocarbon standards has made it possible to account analytically for the compositions of gasolines to the extent of 80-90% in subsequent investigations.

• The first paper of this series is that by G. S. Landsberg and B. A. Kazansky entitled "Determination of the Individual Composition of Straight-run Gasolines by the Combination Method" [1].

TABLE 1
Distribution of Hydrocarbons by Classes

Hydrocarbon class	No. of hydrocarbons detected in gasolines		No. of hydrocarbons determined quantitatively in gasolines		Total No. of hydrocarbons found in the 2 gasolines
	TsK-1	TsK-2	TsK-1	TsK-2	
Paraffins	29	28	16	10	41
Cyclopentanes	8	9	5	4	13
Cyclohexanes	11	9	6	6	11
Aromatics	6	5	6	5	6
Total	54	51	33	25	71

It will be clear from these results that TsK-1 contains an appreciably smaller amount of aromatic hydrocarbons than TsK-2. Also, TsK-1 is richer in branched paraffin hydrocarbons. But the difference between the two gasolines is particularly evident when an appraisal is made of the content of individual groups and classes of hydrocarbons, the total amount of all paraffin and naphthene hydrocarbons being taken as 100%. As will be seen from Table 3, although the overall percent content of paraffin hydrocarbons, dif-

fers little for the two gasolines, the nature of these paraffins differs greatly.

The gasoline TsK-1 contains a considerable amount of branched paraffins, including paraffins containing quaternary carbon atoms (more than 10%, i.e., more than in any of the gasolines that we investigated since), and contains practically no hydrocarbons of normal structure. On the other hand, the gasoline TsK-2 contains a considerable amount of normal paraffins and a small amount of branched hydrocarbons.

TABLE 2
Individual Hydrocarbons Found in the Gasolines TsK-1 and TsK-2

Hydrocarbon	Content (% by wt.)		Hydrocarbon	Content (% by wt.)	
	in TsK-1	in TsK-2		in TsK-1	in TsK-2
Paraffin hydrocarbons					
Butane	0.34	3.82	2,4-Dimethylhexane	1.72	+
Pentane	0.23	5.52	2,5-Dimethylhexane	0.55	+
2-Methylbutane	0.90	3.06	3,4-Dimethylhexane	+	-
Hexane	+	2.41	2,2,3-Trimethylpentane	++	-
2-Methylpentane	0.69	1.86	2,2,4-Trimethylpentane	+	-
3-Methylpentane	0.69		2,3,4-Trimethylpentane	0.57	-
2,2-Dimethylbutane	0.06	-	Nonane	-	+
2,3-Dimethylbutane	0.49	-	3-Methyloctane	-	+
Heptane	-	3.89	4-Methyloctane	-	+
2-Methylhexane	1.56	2.86	4-Ethylheptane	-	+
3-Methylhexane	1.56		3,3-Dimethylheptane	+	-
2,2-Dimethylpentane	1.07	-	3,4-Dimethylheptane	-	++
2,3-Dimethylpentane	4.37	-	3,5-Dimethylheptane	-	++
2,4-Dimethylpentane	1.32	-	4,4-Dimethylheptane	+	-
3,3-Dimethylpentane	++	-	2,3,5-Trimethylhexane	+	+
Octane	++	4.62	2,4,4-Trimethylhexane	-	+
2-Methylheptane	+	+++	3,3,4-Trimethylhexane	+++	++
3-Methylheptane	-	+++	2-Methyl-3-ethylhexane	+	++
3-Ethylhexane	+	+++	3-Methyl-3-ethylhexane	-	+
2,2-Dimethylhexane	2.85	-	3-Methyl-4-ethylhexane	-	+
2,3-Dimethylhexane	-	+			
			Total	19.0	28.0
Cyclopentane hydrocarbons					
Cyclopentane	0.10	0.60	Propylcyclopentane	+	-
Methylcyclopentane	0.08	1.92	Isopropylcyclopentane	++	-
Ethylcyclopentane	-	++	1-Ethyl-1-methylcyclopentane	-	+
cis-1,2-Dimethylcyclopentane	-	0.90	1-Ethyl-2-methylcyclopentane	-	++
trans-1,2-Dimethylcyclopentane	-	1.43	1 ^c ,2 ^c ,3 ^c -Trimethylcyclopentane	+	-
1,3-Dimethylcyclopentane	2.77	-	1 ^c ,2 ^t ,3 ^c -Trimethylcyclopentane	2.62	+
			1 ^c ,2 ^c ,3 ^t -Trimethylcyclopentane	0.70	+
			Total	6.3	4.9

TABLE 2 -- (continued)

Hydrocarbon	Content (% by wt.)		Hydrocarbon	Content (% by wt)	
	in TsK-1	in TsK-2		in TsK-1	in TsK-2
Cyclohexane hydrocarbons					
Cyclohexane	0.53	2.03	Cyclohexane hydrocarbons	5.64	1.89
Methylcyclohexane	1.49	5.67	C ₉ H ₁₈ including:		
Ethylcyclohexane	1.28	2.98			
1,1-Dimethylcyclohexane	++	+++	1-Ethyl-2-methylcyclohexane	+	+
1,2-Dimethylcyclohexane	2.34	2.01	1-Ethyl-3-methylcyclohexane	+	+
1,3-Dimethylcyclohexane	2.15	2.46	1-Ethyl-4-methylcyclohexane	+	-
1,4-Dimethylcyclohexane	0.29	0.30	1,2,4-Trimethylcyclohexane	+	-
Total				13.7	17.3
Aromatic hydrocarbons					
Benzene	0.19	0.43	o-Xylene	0.08	0.19
Toluene	0.11	1.36	m-Xylene	0.06	1.54
Ethylbenzene	0.20	1.36	Cumene	0.14	-
Total				0.8	4.9
Accounted for quantitatively				39.8	55.1
Not accounted for quantitatively, but partially accounted for qualitatively				37.1	20.7
Losses				16.8	21.7
Residues in flasks after fractionations				6.3	2.5
Total				100.0	100.0

NOTE. + indicates that the hydrocarbon was detected qualitatively in one fraction; ++ indicates that it was either detected in two fractions or was found in considerable amount in one fraction; +++ indicates that it was either detected in three fractions, or was detected in two, there being a considerable amount in one of these.

TABLE 3

Composition by Groups of the Paraffin-Naphthene Parts of the Gasolines TsK-1 and TsK-2 (% on the Gasoline)

Hydrocarbons	Gasolines	
	TsK-1	TsK-2
Normal paraffins	1.46	40.33
Paraffins having tertiary carbon atoms	37.01	15.49
Paraffins having quaternary carbon atoms	10.22	0
Cyclopentanes	16.09	9.66
Cyclohexanes	35.22	34.52

given in Tables 4 and 5 and in Fig. 1. It will be seen already by comparison of these curves that these gasolines differ considerably in chemical nature.

The main fractions of the two gasolines had the following properties: AK-1 - n_D^{20} 1.4150; d_4^{20} 0.7489; AK-2 - n_D^{20} 1.4110; d_4^{20} 0.7433.

The Fractions K_1 , L, and A, i.e., all that came over below 150°, comprise the "whole gasoline", TsK-1 (2396.6 g) and TsK-2 (3967.5 g).

Investigation of the Gases and Light Fractions (K_1 and L). By fractionation of the gaseous part of K_1 -K-1 through a Podbiełniak column it was established that the gas consisted of butane. From the course of the fractionation of LK-1 and the properties of the fractions obtained it was shown that LK-1 consisted of isopentane,

EXPERIMENTAL

Characteristics of Samples of Kazanbulak Petroleum. Petroleum No. 1 was a heavy viscous liquid having d_4^{20} 0.9127. Petroleum No. 2 was a liquid of relatively low viscosity, d_4^{20} 0.8330.

The Wide Cuts ShK-1 and ShK-2 and Their Fractionation. The gasoline samples referred to as wide cuts had the following properties: ShK-1, n_D^{20} 1.4345; d_4^{20} 0.7828; ShK-2, n_D^{20} 1.4200; d_4^{20} 0.7393.

The cuts were distilled through a 25-plate column, and the results of the fractionation are

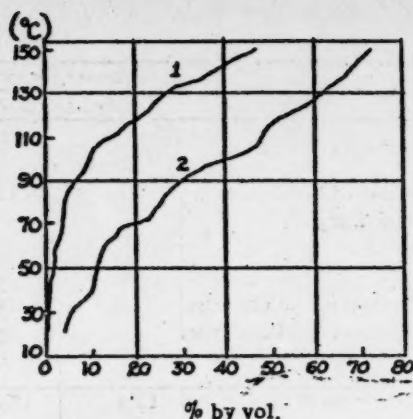


Fig. 1. Fractionation curves for the wide cuts: 1) ShK-1; 2) ShK-2.

TABLE 4
Results of the Fractionation of the Gasoline ShK-1

Name of fraction	Boiling range (°C at 760mm)	Weight (g)	Content of fraction (% by weight)	
			in ShK-1	in TsK-1
Taken for fractionation	—	5644.0	100.0	—
K _I K-1 + LK-1 - light fraction with gaseous part	up to 53.0	46.9	0.8	1.96
AK-1 - main fraction	53.0-150.0	2349.7	41.6	98.04
O _{II} K-1 - residue	—	3156	55.9	—
Losses	—	91	1.7	—

TABLE 5
Results of the Fractionation of the Gasoline ShK-2

Name of fraction	Boiling range (°C at 760 mm)	Weight (g)	Content of fraction (% by weight)	
			in ShK-2	in TsK-2
Taken for fractionation	—	5552.0	100.0	—
K _I K-2 - gaseous part	—	166.7	3.0	4.20
LK-2 - light fraction	up to 50.2	396.8	7.1	10.00
AK-2 - main fraction	50.2-150.0	3404.0	61.3	85.80
O _{II} K-2 - residue	—	1520	27.4	—
Losses	—	64	1.2	—

TABLE 6
Chromatographic Separation of Fractions AK-1 and AK-2

Fraction	Amt. of fraction taken (g)	Results of separation							
		Aromatics (B)			Paraffin naphthene part (C)			Losses	
		(g)	(% in A)	(% in Ts)	(g)	(% in A)	(% in Ts)	(g)	(% in A) (% in Ts)
AK-1	1305.3	10.65	0.82	0.80	1227.0	94.0	92.16	67.65	5.2 5.08
AK-2	1008.4	59.75	5.90	5.08	879.0	87.2	74.79	69.65	6.9 5.93

ethylbenzene, and Fraction IV to cumene. Fractions III and IV were investigated with the aid of Raman spectra. It was found that Fraction III of the aromatics BK-1 contained 60% (0.20% on TsK-1) of ethylbenzene, 22% (0.07% on TsK-1) of o-xylene, and 18% (0.06% on TsK-1) of m-xylene; Fraction IV contained 5% (0.01% on TsK-1) of o-xylene and 95% (0.14% on TsK-1) of isopropylbenzene. Fraction III of the aromatics BK-2 contained 44%

pentane, 2,2-dimethylbutane, and cyclopentane (Table 2). In the gaseous part of K_IK-2 butane and some propane were found; in LK-2 isopentane and pentane were found (Table 2).

Separation of Aromatic Hydrocarbons from the Mixture of Paraffins and Naphthenes in the Main Fractions (A). In order to free the A fractions from aromatics, they were subjected to chromatographic analysis in columns filled with silica gel. As a result there were obtained aromatic fractions (B) and fractions consisting of paraffin and naphthenic hydrocarbons (C). The results of the separation are given in Table 6.

Investigation of the Aromatics (B). The aromatics that had been separated by chromatographic adsorption were fractionated through a column of about 40-plate efficiency. The results of the fractionation are given in Tables 7 and 8.

It will be seen from Tables 7 and 8 that Fraction I corresponds to benzene, Fraction II to toluene, Fraction III to xylenes and

TABLE 7
Fractionation of the Aromatics BK-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% by wt.)	
					in BK-1	in TsK-1
Taken for fractionation		10.55			100.0	0.80*
I	78.1 - 100.9	2.55	1.4900	0.8533	24.2	0.19
II	100.9 - 129.7	1.5	1.4919	0.8580	14.2	0.11
III	129.7 - 145.2	4.4	1.4945	—	41.7	0.33
IV	145.2 - 154.0	2.0	1.4900	0.8604	19.0	0.15
Residue		0.05	—	—	0.5	0.01
Losses		0.05	—	—	0.4	0.01

TABLE 8
Fractionation of the Aromatics BK-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (%) by wt.)	
					in BK-2	in TsK-2
Taken for fractionation		19.1			100.0	5.08
I	78.8 - 102.1	1.6	1.4923	0.8619	8.4	0.43
II	102.1 - 128.9	5.1	1.4947	0.8624	26.7	1.36
III	128.9 - 141.8	9.6	1.4973	0.8650	50.3	2.55
Residue		2.0	1.4980	—	10.5	0.53
Losses		0.8	—	—	4.2	0.21

TABLE 9
Chromatographic Separation of the Catalyzates GK-1 and GK-2

Fraction	Amount of fraction taken (g)	Results of separation								
		Aromatics (P)			Paraffin-cyclopentane part			Losses		
		(g)	(% in D)	(% in Ts)	(g)	(% in D)	(% in Ts)	(g)	(% in D)	(% in Ts)
GK-1	339.8	51.2	15.1	12.81	275.7	81.1	68.84	12.9	3.8	3.23
GK-2	296.0	74.3	25.1	16.58	200.4	67.7	44.72	21.3	7.2	4.76

TABLE 10
Fractionation of the Aromatics DK-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction in DK-1 (% by wt.)	Content of corresponding cyclohexane hydrocarbons in TsK-1 (%)
Taken for fractionation		51.6			100.0	
I	77.8 - 103.2	1.7	1.4664	0.8150	3.3	0.45
II	103.2 - 129.7	4.8	1.4683	0.8241	9.3	1.27
III	129.7 - 146.9	22.1	1.4921	0.8578	42.8	5.80
IV	146.9 - 166.6	9.6	1.4988	0.8657	18.6	2.50
Residue		13.0	—	—	25.2	3.39
Losses		0.4	—	—	0.8	0.10

(1.36% on TsK-2) of ethylbenzene, 6% (0.19% on TsK-2) of o-xylene, and 50% (1.54% on TsK-2) of m-xylene; as the refractive indices of Fraction III and of the residue were nearly equal, it was assumed that they were of identical composition, and in this way the residue was taken into account in the analysis of the aromatics of the gasoline TsK-2. On the basis of all the results obtained, the contents of aromatic hydrocarbons in the whole gasolines were calculated and are given in Table 2.

* In this and succeeding tables the amount indicated is expressed as percent content of the whole of the given fraction in TsK 1 and TsK 2 and not of the portion taken for investigation.

TABLE 11

Fractionation of the Aromatics DK-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction in DK-2 (% by wt.)	Content of corresponding cyclohexane hydrocarbons in TsK-2 (%)
Taken for fractionation		74.8			100.0	
I	77.8-100.9	7.5	1.4916	0.8626	10.03	1.79
II	100.9-129.9	24.0	1.4917	0.8588	32.09	5.67
III	129.9-141.6	25.5	1.4949	0.8602	34.09	5.97
IV	141.6-146.2	5.9	1.5012	0.8731	7.89	1.39
V	146.2-166.7	5.6	1.4970	0.8680	7.49	1.30
Residue		4.2	—	—	5.61	0.98
Losses		2.1	—	—	2.80	0.50

TABLE 12

Fractionation of the Paraffin-Cyclopentane Part of EK-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	Content of fraction (% by wt.)		n_D^{20}	d_4^{20}	Aniline point (°C)
			in EK-1	in TsK-1			
Taken for fractionation		213.8	100.0	68.84			
I	48.8- 67.5	5.8	2.7	1.87	1.3761	0.6626	—
II	67.5- 88.0	8.5	4.0	2.74	1.3907	0.6953	64.5
III	88.0- 97.0	26.1	12.2	8.41	1.3982	0.7119	61.45
IV	97.0-107.2	17.2	8.0	5.54	1.4103	0.7439	58.65
V	107.2-110.0	10.7	5.0	3.44	1.4067	0.7331	64.7
VI	110.0-115.0	13.6	6.4	4.38	1.4063	0.7281	65.8
VII	115.0-120.0	20.5	9.6	6.60	1.4110	0.7372	62.1
VIII	120.0-125.0	15.0	7.0	4.83	1.4193	0.7583	56.4
IX	125.0-130.0	6.7	3.1	2.16	1.4200	0.7606	—
X	130.0-136.0	23.6	11.0	7.60	1.4160	0.7480	65.2
XI	136.0-138.0	25.6	12.0	8.24	1.4201	0.7575	65.2
XII	138.0-143.7	19.8	9.3	6.37	1.4225	0.7617	61.2
XIII	143.7-146.4	6.9	3.2	2.22	1.4287	0.7775	—
Residue		8.3	3.9	2.67			
Losses		5.5	2.6	1.77			

Dehydrogenation of Cyclohexane Hydrocarbons. The paraffin-naphthene parts of the gasolines (401.5 g of VK-1 and 366.7 g of VK-2) were dehydrogenated in order to convert the cyclohexane hydrocarbons into aromatics. Before dehydrogenation the C fractions had the following properties: VK-1: n_D^{20} 1.4145; d_4^{20} 0.7482; aniline point 61.3°; VK-2: n_D^{20} 1.4109; d_4^{20} 0.7349; aniline point 58.5°. Dehydrogenation was carried out over a specially prepared catalyst. The catalyzates obtained — 369.8 g of GK-1 (84.88% on TsK-1) and 323.9 g of GK-2 (66.06% on TsK-2) — had the following properties: GK-1: n_D^{20} 1.4254; d_4^{20} 0.7609; GK-2: n_D^{20} 1.4270; d_4^{20} 0.7548. The losses during dehydrogenation were 6.58% for TsK-1 and 7.71% for TsK-2.

Separation of the Catalyzates (D) into Aromatic Hydrocarbons and a Mixture of Paraffins and Cyclopentanes. The catalyzates D were separated by means of chromatographic adsorption into aromatic fractions (E) and fractions consisting of paraffin and cyclopentane hydrocarbons (F). The results of the separation are given in Table 9.

Investigation of the Aromatics (E). The aromatics separated were fractionally distilled through a column. The results of the fractionation and the properties of the fractions are shown in Tables 10 and 11.

It will be seen from Table 10 that Fraction I corresponds to benzene. Fractions III and IV were investigated optically, and it was found that Fraction III contained 36% of o-xylene, 37% of m-xylene, 5% of p-xylene, and 22% of ethylbenzene.

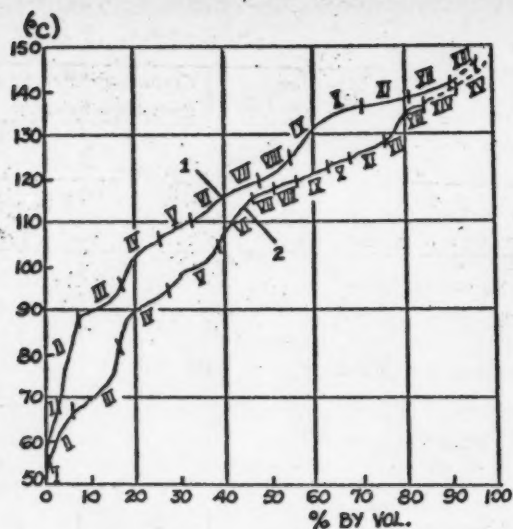


Fig. 2. Fractionation curves for the fractions EK-1 (1) and EK-2 (2).

TABLE 13

Fractionation of the Paraffin-Cyclopentane Part of EK-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	Content of fraction (% by wt.)		n _D ²⁰	d ₄ ²⁰	Aniline point (°C)
			in EK-2	in TsK-2			
Taken for fractionation		198.6	100.0	45.80*			
I	36.1- 54.0	4.0	2.0	0.92	1.3888	0.6991	—
II	54.0- 66.0	9.9	5.0	2.29	1.3768	0.6659	66.8
III	66.0- 80.0	20.9	10.5	4.81	1.3913	0.6985	54.95
IV	80.0- 95.0	20.7	10.4	4.76	1.4000	0.7174	58.1
V	95.0-104.0	21.1	10.6	4.86	1.3967	0.7052	62.25
VI	104.0-115.0	14.3	7.2	3.30	1.4095	0.7377	68.0
VII	115.0-117.6	6.6	3.3	1.51	1.4041	0.7212	66.9
VIII	117.6-118.0	11.7	5.9	2.70	1.4042	0.7172	66.8
IX	118.0-122.0	9.9	5.0	2.29	1.4072	0.7261	64.35
X	122.0-124.5	9.7	4.9	2.24	1.4063	0.7249	64.75
XI	124.5-128.0	15.5	7.8	3.57	1.4033	0.7163	67.4
XII	128.0-133.5	6.6	3.3	1.51	1.4115	0.7352	65.0
XIII	133.5-137.0	11.7	5.9	2.70	1.4181	0.7518	67.0
XIV	137.0-140.0	7.1	3.6	1.65	1.4188	0.7514	64.6
XV	140.0-148.8	15.9	8.0	3.66	1.4141	0.7392	68.4
Residue		6.4	3.2	1.47			
Losses		6.6	3.4	1.56			

* Including the residue from the fractionation of the light fraction LK-2.

About 10% of *o*-xylene was found in Fraction IV, and it was shown that 1-ethyl-2-methylbenzene and 1-ethyl-3-methylbenzene were also present in this fraction. The contents of the cyclohexane hydrocarbons corresponding to the aromatic hydrocarbons found are given in Table 2.

It follows from Table 11 that Fraction I corresponds to benzene, and Fraction II to toluene. Fractions III, IV, and V were investigated with the aid of Raman spectra. Fraction III was found to contain 40% of *m*-xylene, 10% of *o*- and *p*-xylenes and 50% of ethylbenzene. Fraction IV contained 95% of *o*-xylene and 5% of *m*-xylene. In Fraction V 30% of *o*-xylene was found and it was shown that 1-ethyl-4-methyl-, 1-ethyl-2-methyl-, and 1-ethyl-3-methylbenzenes were present. The contents of the corresponding cyclohexane hydrocarbons are given in Table 2.

Investigation of the Paraffin-Cyclopentane Fractions (F). The F fractions separated by chromatographic adsorption had the following properties: EK-1 n_D^{20} 1.4131; d_4^{20} 0.7422; EK-2 n_D^{20} 0.7202. The F fractions were fractionated through a column having an efficiency of about 50 theoretical plates. As a preliminary, the fractionation curves were determined for these fractions by fractionation of separate 80-ml portions, and these curves are shown in Fig. 2. The F fractions (270-280 ml) were then fractionated into narrow fractions, which were investigated with the aid of their Raman spectra.

TABLE 14

Results of the Optical Investigation of Narrow Fractions of the Paraffin-Cyclopentane Part of EK-1

Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)		Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)	
	in the fraction	in TsK-1		in the fraction	in TsK-1
Fraction I			1,3-Dimethylcyclopentane	50	2.77
2,3-Dimethylbutane	26	0.49	Methylcyclohexane	4	0.22
2-Methylpentane	74*	0.69	Fraction V		
3-Methylpentane		0.69	2,2-Dimethylhexane	20	0.69
Fraction II			1 ^c ,2 ^t ,3 ^c -Trimethylcyclopentane	34	1.17
2,4-Dimethylpentane	48	1.32	2,4-Dimethylhexane	12	0.41
2,2-Dimethylpentane	39	1.07	2,5-Dimethylhexane	16	0.55
Cyclohexane	3	0.08	Fraction VI**		
Methylcyclopentane	3	0.08	1 ^c ,2 ^t ,3 ^c -Trimethylcyclopentane	33	1.45
Fraction III			1 ^c ,2 ^c ,3 ^t -Trimethylcyclopentane	16	0.70
2,3-Dimethylpentane	52	4.37	2,4-Dimethylhexane	30	1.31
2-Methylhexane	37*	1.56	2,3,4-Trimethylpentane	13	0.57
3-Methylhexane		1.56			
Fraction IV					
2,2-Dimethylhexane	39	2.16			

* About equal amounts.

** The remaining fractions were investigated qualitatively (see Table 2).

TABLE 15

Results of the Optical Investigation of Narrow Fractions of the Paraffin-Cyclopentane Part of EK-2

Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)		Hydrocarbons found by the optical method	Content of the hydrocarbon (% by wt.)	
	in the fraction	in TsK-2		in the fraction	in TsK-2
Fraction I			Fraction V		
Pentane	35*	0.32	Heptane	80	3.89
Cyclopentane	65	0.60	cis-1,2-Dimethylcyclopentane**	18	0.90
Fraction II			Fraction IX***		
2-Methylpentane	81**	1.86	Octane	30	0.69
3-Methylpentane			Fraction X		
Fraction III			Octane	60	1.34
Hexane	50	2.41	Fraction IX		
Methylcyclopentane	40	1.92	Octane	60	2.14
Fraction IV			Fraction XII		
2-Methylhexane	60	2.86	Octane	30	0.45
3-Methylhexane					
trans-1,2-Dimethylcyclopentane	30	1.43			
Cyclohexane	5	0.24			

* The quantitative optical analysis was made difficult by the small volume of the fraction. It was shown that cyclopentane was undoubtedly in excess. The quantitative estimation was made on the basis of the refractive indices and specific volumes of binary mixtures of pentane and cyclopentane.

** 3-Methylpentane predominated.

*** The Fractions VI-VIII and XIII-XV were investigated qualitatively (see Table 2).

Tables 12-15 show the results of the fractionation of the F fractions into narrow fractions, the physical properties of these fractions, and the results of their optical analysis.

On the basis of all of the results obtained, the contents of paraffin and cyclopentane paraffins in the whole gasolines given in Table 2 were calculated. Table 2 forms the general balance sheet for the whole investigation.

SUMMARY

1. With the aid of the combination method for the investigation of the individual hydrocarbon composition of straight-run gasolines, a study has been made of gasoline fractions derived from two petroleum originating from two horizons at Kazanbulak. In the fractions boiling below 150° more than 70 individual hydrocarbons have been detected qualitatively. It was found possible to account quantitatively for 55% of one of the gasolines and for 40% of the other.

2. It has been shown that, in spite of the closeness of the strata from which these petroleum were obtained, the chemical nature of the hydrocarbons forming their gasoline fractions differs very greatly.

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Tables 12-15 show the results of the fractionation of the 7 fractions into narrow fractions and physical properties of some of these and the results of their physical analysis.

On the basis of 10 of the results obtained the content of paraffins and cyclopentane paraffins in the whole fractions given in Table 1 is calculated. Table 2 shows the general balance sheet for the whole investigation.

SUMMARY

1. With the aid of the composition method for the investigation of the liquid phase hydrocarbon composition of straight-run gasoline, a study was made of gasoline fractions derived from two petroleum refineries. From one refinery of Kazakhstan in the fractionation of the whole gasoline, it was found possible to separate approximately for 80% of one of the paraffins and for 95% of the other.
2. It has been shown that in spite of the complexity of the liquid phase which these hydrocarbons are characterized the results of the hydrocarbon fractionation from two petroleum refineries are very similar.

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LITERATURE CITED

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES BY THE COMBINATION METHOD

COMMUNICATION 3. SURAKHAN GASOLINES

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In this paper we give the results of an investigation of two gasoline samples derived respectively from Surakhan first-grade and oil-grade petroleums. The previously described procedure was employed [1], as in the case of our investigation of two gasolines from Kazanbulak petroleums [2], the only difference being that the "whole" gasolines were not separated by laboratory distillation of the petroleums, but were taken from large-scale running.

As a result of detailed development work on the analytical procedure, in particular on the preparation of an active and reliable catalyst, and as a result also of increase in the number of available hydrocarbon standards for spectrum examination, it was possible in this investigation greatly to increase the extent to which the individual components of the gasolines could be accounted for quantitatively, and also to reduce losses considerably, as compared with the investigation described in the previous paper [2].

Both of the Surakhan gasolines contained a certain amount of sulfur compounds, and purification from these was not provided for in our procedure. This difficulty, however, was readily overcome, and the presence of sulfur compounds was without effect on the results of the investigation.

The gasoline derived from Surakhan first-grade petroleum, which will be denoted hereafter by TsS-1, was accounted for quantitatively to the extent of 77.8%, and the gasoline from Surakhan oil-grade petroleum, denoted hereafter by TsS-2, was accounted for quantitatively to the extent of 84.0%. The symbols used to denote the fractions are the same as those used in the papers cited above [1, 2].

TABLE 1
Distribution by Classes of Hydrocarbons Found

Hydrocarbon class	No. of hydrocarbons detected in gasoline		No. of hydrocarbons determined quantitatively in gasoline		Total No. of hydrocarbons found in the two
	TsS-1	TsS-2	TsS-1	TsS-2	
Paraffins	21	19	18	19	25
Cyclopentanes	8	8	7	8	10
Cyclohexanes	7	8	7	8	8
Aromatics	6	6	6	6	6
Total	42	41	38	41	49

In the two gasolines, 49 different hydrocarbons were detected. The distribution of these by classes is given in Table 1.

As will be seen from Table 1, the number of hydrocarbons accounted for quantitatively and qualitatively is practically the same for each gasoline. The number of hydrocarbons in each class is also the same for the two gasolines. The natures of these hydrocarbons, however, are considerably different for the two gasolines, and these differ considerably in their individual hydrocarbon compositions. This difference in composition will be readily seen from Table 2, in which the amounts of the individual hydrocarbons found in the gasolines under investigation are given.

TABLE 2

Individual Hydrocarbons found in the Gasolines TsS-1 and TsS-2

Name of hydrocarbon	Content (% by wt.)		Name of hydrocarbon	Content (% by wt.)	
	in TsS-1	in TsS-2		in TsS-1	in TsS-2
Paraffin hydrocarbons					
Methane	—	0.03	2,2-Dimethylpentane	0.28	0.22
Propane	0.08	—	2,4-Dimethylpentane	1.13	0.43
Butane	0.71	0.08	3,3-Dimethylpentane	0.68	—
Pentane	0.55	0.94	2,2,3-Trimethylbutane	0.28	0.11
2-Methylbutane	0.80	0.67	Octane	—	5.7 ^a
Hexane	0.62	3.82	2-Methylheptane	+?	5.70
2-Methylpentane	1.67	3.07	3-Methylheptane	+?	3.69
3-Methylpentane	0.60		4-Methylheptane	+	—
2,2-Dimethylbutane	0.44	0.19	2,2-Dimethylhexane	0.49	—
2,3-Dimethylbutane	1.07	0.38	2,3-Dimethylhexane	+	—
Heptane	+	6.40	2,4-Dimethylhexane	0.49	0.39
2-Methylhexane	3.16	3.01	2,5-Dimethylhexane	0.49	—
3-Methylhexane	1.91	2.01	Total	15.4	36.9
Cyclopentane hydrocarbons					
Cyclopentane	0.06	0.76	Ethylcyclopentane	+	0.39
Methylcyclopentane	4.59	2.88	1 ^c ,2 ^t ,3 ^c -Trimethylcyclopentane	2.05	—
1,1-Dimethylcyclopentane	0.96	—	1,2,4-Trimethylcyclopentane	3.45	4.28
cis-1,2-Dimethylcyclopentane	5.49	—	Propylcyclopentane	—	0.79
trans-1,2-Dimethylcyclopentane		3.01	Isopropylcyclopentane	—	0.53
1,3-Dimethylcyclopentane	1.91	2.00	Total	18.5	14.6
Cyclohexane hydrocarbons					
Cyclohexane	7.37	4.57	1,4-Dimethylcyclohexane	1.12	1.71
Methylcyclohexane	20.05	12.53	Ethylcyclohexane	2.23	2.28
1,1-Dimethylcyclohexane	2.99	1.20	1,1,3-Trimethylcyclohexane	—	0.52
1,2-Dimethylcyclohexane	1.12	2.19	Other cyclohexane hydrocarbons	2.52	0.70
1,3-Dimethylcyclohexane	5.68	3.33	of composition C ₉ H ₁₈		
Total			Total	43.1	29.0
Aromatic hydrocarbons					
Benzene	0.04	0.88	m-Xylene	0.18	0.59
Toluene	0.18	1.00	p-Xylene	0.12	0.25
o-Xylene	0.03	0.32	Ethylbenzene	0.28	0.45
Total			Total	0.8	3.5
Total hydrocarbons accounted for				77.8	84.0
Not accounted for quantitatively, but partially determined qualitatively				9.7	4.8
Losses				5.9	7.2
Residues in flasks from fractionations				6.6	4.0
Total				100.0	100.0

* + — hydrocarbon detected qualitatively.

+? — this hydrocarbon may be present.

The gasoline from the first-grade petroleum contained about half as much paraffin hydrocarbons as that derived from the oil-grade petroleum. In the gasoline TsS-1, mainly branched paraffins were found (13.4% out of a total paraffin content of 15.4%), but in the gasoline TsS-2 approximately equal amounts of normal and branched paraffins were present (17.0% and 19.9%). There was a greater amount of paraffins having quaternary carbon atoms in the gasoline TsS-1 (2.05%) than in the gasoline TsS-2 (0.52%), but the greater part of the branched paraffins did not contain quaternary carbon atoms.

When the compositions of the gasolines are examined a group at a time, each group consisting of hydrocarbons of a particular molecular weight, it will be seen that in both gasolines all possible isomeric C_5 and C_6 hydrocarbons were present, apart from neopentane. In the C_7 group, heptane was found in the gasoline TsS-2, but was only detected qualitatively in the gasoline TsS-1; among the heptane isomers, 2,3-dimethylpentane and 3-ethylpentane were absent in both gasolines. Among the C_8 hydrocarbons, octane was found only in the gasoline TsS-2; hydrocarbons having one side chain were represented only by 2- and 3-methylheptanes, and there were only three having two side chains, namely 2,2-, 2,4-, and 2,5-dimethylhexanes; no highly ramified octane isomers were present. No C_9 hydrocarbons were found in either gasoline; it may therefore be supposed that the high-boiling part of the gasolines consisted mainly of naphthenic hydrocarbons.

An examination of the cyclopentane hydrocarbons indicates that the gasoline TsS-1 contained a considerably greater amount of disubstituted compounds (8.4%) than the gasoline TsS-2 (5.0%), in which the distribution of cyclopentane hydrocarbons according to weight was more even. The content of cyclohexane hydrocarbons, which was high in both of the gasolines, was about 50% higher in the gasoline derived from the first-grade petroleum than in that derived from the oil petroleum. The high content of methylcyclohexane (20.05% in TsS-1 and 12.53% in TsS-2) is particularly notable. The content of aromatic hydrocarbons was very low (0.8% and 3.5%), and was higher in the gasoline having the lower content of cyclohexanes (TsS-2).

EXPERIMENTAL

All of the fractions obtained in the course of the investigation were denoted by symbols, in accordance with the scheme given in a previous paper [1].

The original gasolines were fractionated through a column of 25-plate efficiency. The results of the fractionations and the properties of the original gasolines are given in Tables 3 and 4 and Fig. 1. In view of the fact that, as the fractionation showed, both samples were light gasolines, the final calculation of individual composition was based on the amounts of original gasolines. In this case, therefore, the original gasolines were "whole" gasolines (Ts).

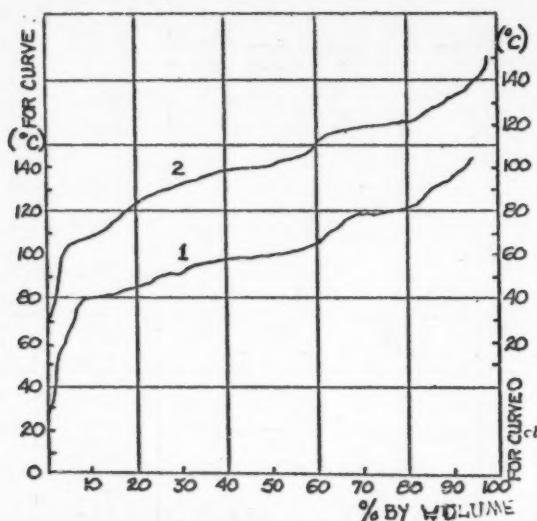


Fig. 1. Fractionation curves of the fractions ShS-1 (1) and ShS-2 (2).

In the fractionation of the original gasolines, three fractions were collected: the gaseous part K_1 (the condensate formed in traps cooled to -70°); the light fraction L (distillate obtained up to the temperature at which the first traces of benzene can be detected (positive formolite test)); and the fraction A (from the tail of Fraction L to 150°).

Investigation of the Gases in the Light Fractions (K_1 and L). In the case of the fraction K_1 S-1, 6.6 g was taken for fractionation through a Podbielniak column, and it yielded 0.4 g of propane, 3.6 g of butane, and 2.6 g of high-boiling residue. It follows that the gasoline TsS-1 contained 0.08% of propane and 0.71% of butane. Owing to a mishap, the residue was not isolated from the main portion of the gas K_1 .

No gas was found in the fraction LS-1; so that in this case the light fraction LS-1 corresponded to the debutanated light fraction MS-1.

The fractionation of the light part was carried out with a 50-plate column. Simultaneously with the collection of fractions, the fractionation curve was determined. Since all of the fractions obtained

contained small amounts (less than 0.1%) of sulfur compounds, the fractions were passed through silica gel in order to remove these. The sulfur compounds were thus separated from the hydrocarbons, and the former collected in the alcoholic part. The amounts of the fractions obtained and their properties after they had been freed from sulfur compounds are given in Table 5.

Since the mean boiling points, specific gravities, and refractive indices of Fractions I and II correspond respectively to the corresponding constants of 2-methylbutane (b.p. 27.85°; n_D^{20} 1.3537; d_4^{20} 0.6197), and pentane (b.p. 36.07°; n_D^{20} 1.3575; d_4^{20} 0.6262), the amounts of these fractions give the contents of these hydrocarbons in the gasoline.

Fraction III, as a study of its Raman spectra showed, contained 85% of 2,2-dimethylbutane and 15% of cyclopentane; from which it follows that the content of 2,2-dimethylbutane in the whole gasoline was 0.32%, and that of cyclopentane was 0.06%.

The residue from the fractionation of MS-1, which contained sulfur compounds, was passed for purification through silica gel, and was then united with the fraction VS-1 (see below).

TABLE 3

Fractionation of the Original Gasoline TsS-1

Fraction	Boiling range (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction in TsS-1 (% by wt.)
Taken for fractionation		2132	1.4162	0.756	100.0
K ₁ S-1 (gaseous part)	—	28.4	—	—	1.3
LS-1 (light fraction)	27.3-57.6	51.0	—	—	2.4
AS-1 (main fraction)	57.6-150.0	1970.0	1.4148	0.7496	92.4
Residue	—	63.0	—	—	3.0
Losses	—	19.6	—	—	0.9

TABLE 4

Fractionation of the Original Gasoline TsS-2

Fraction	Boiling range (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Content of fraction in TsS-2 (% by wt.)
Taken for fractionation		1248	1.4097	0.7335	100.0
K ₁ S-2 (gaseous part)	—	6.6	—	—	0.5
LS-2 (light fraction)	29.5- 48.4	21.4	—	—	1.7
AS-2 (main fraction)	48.4-149.8	1186.8	1.4100	0.7358	95.1
Residue	—	8.6	—	—	0.7
Losses	—	24.6	—	—	2.0

TABLE 5

Fractionation of MS-1, and the Properties of the Fractions

Fraction No.	Boiling range (°C at 760 mm)	Weight (g)	n_D^{20}	d_4^{20}	Aniline point (°C)	Content (% by wt.)	
						in MS-1	in TsS-1
Taken for fractionation		51.0				100.00	
I	25.7-32.0	16.9	1.3533	0.6202	76.9	33.14	0.80
II	32.0-42.1	11.7	1.3577	0.6280	70.3	22.94	0.55
III	42.1-55.2	8.1	1.3763	0.6617	65.6	15.88	0.38
Residue		10.2	—	—	—	20.00	0.48
Losses		4.1	—	—	—	8.04	0.19

For the investigation of the fraction K_1S-2 , 6.6 g was taken. Fractionation through a Podbielniak column yielded 0.39 g of methane, 0.12 g of intermediate fraction (C_2 and C_3 hydrocarbons), and 0.99 g of butane. It follows that for the whole gasoline, the methane content was 0.03% and the butane content was 0.08%.

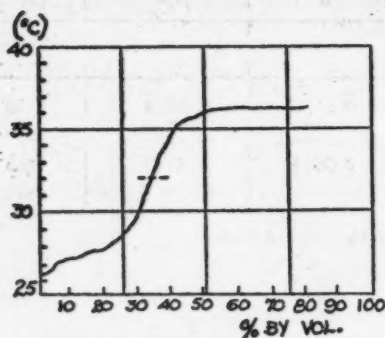


Fig. 2. Fractionation curve for the fraction MS-2.

As there was no gas component in LS-2, the residue from the fractionation of the gas K_1 was united to LS-2. Traces of sulfur compounds were present in MS-2, and the fraction was therefore passed through silica gel. The losses and the sulfur compounds amounted in all to 1.0 g. The light part, purified in this way, was fractionated through a 50-plate column. The results of the fractionation and the amounts of the fractions are shown in Table 6 and Fig. 2.

The average boiling points, specific gravities, and refractive indices of Fractions I and II corresponded to 2-methylbutane and pentane. The content of 2-methylbutane in the whole gasoline was 0.64%, and the pentane content was 0.91%. Owing to the small amount of residue, this was not investigated optically.

Separation of Aromatics from the Mixture of Paraffins and Naphthenes. The A fractions were subjected to chromatographic separation on silica gel, an aromatic part (B) and a paraffin-naphthene part (C) being isolated. The results of the separation for the two gasolines are given in Table 7.

Both the actual figures for the separated amounts of B and C and the corrected figures are given in Table 7; the corrected figures were obtained by addition of the amounts of the fractions used in tests for aromatic hydrocarbons and for refractive index determinations (which are not losses from the point of view of analysis) to the amounts actually separated. The true losses, which are given at the end of Table 7, amounted to a fraction of one percent.

Investigation of the Aromatics (B). The aromatic hydrocarbons separated with the aid of silica gel were fractionated through a 40-plate column. At the same time the fractionation curve was determined, and fractions were collected corresponding to benzene, toluene, and the xylenes. Fraction III was investigated with the aid of Raman spectra. The results of the fractionations, the properties of the fractions, and the results of the optical analysis are given in Tables 8 and 9. The fractionation curve for BS-1 is given in Fig. 3.

The contents of aromatic hydrocarbons in the whole gasolines, calculated on the basis of these results, are given in Table 2.

Dehydrogenation of Cyclohexane Hydrocarbons. The paraffin-naphthene parts (C) of the gasolines were dehydrogenated in order to convert the cyclohexane hydrocarbons into aromatics, so that they could be separated and their qualitative and quantitative composition determined. Before dehydrogenation the C fractions had the following properties: VS-1 - n_D^{20} 1.4139; d_4^{20} 0.7485; aniline point 50.2°; VS-2 - n_D^{20} 1.4067; d_4^{20} 0.7314; aniline point 56.7°.

The amounts of the C fractions taken for dehydrogenation and the amounts of the catalyzates obtained (D fractions) are given in Table 10. Again, as in Table 7, we give the actual and corrected amounts of D which were obtained by the introduction of corrections for the amounts of the D fractions used for refractive index determinations carried out during the dehydrogenation.

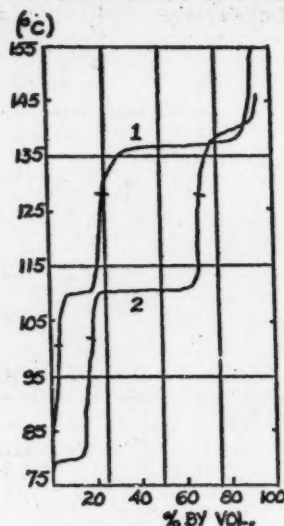


Fig. 3. Fractionation curves for the fractions BS-1 (1) and DS-1 (2).

TABLE 6

Fractionation of MS-2, and Properties of Fractions

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Aniline point (°C)	Content (% by wt.)	
						In MS-2*	in TsS-2
Taken for fractionation		24,5				100,0	
I	26.0-32.0	7.9	1.3533	0.6195	76.3	31.0	0.64
II	32.0-36.2	11.1	1.3568	0.6269	70.1	43.6	0.91
Residue		3.2	1.3857	0.6831	49.7	12.5	0.26
Losses		2.3	—	—	—	9.0	0.15

* Calculated on the amount of M before removal of sulfur compounds, i.e., on 25.9 g.

TABLE 7

Chromatographic Separation of A Fractions

Fraction No.	Wt. of fraction (g)	Results of separation										
		aromatics (B)				paraffin-naphthene part (C)				losses		
		actual (g)	corr. (g)	in A (%)	in Ts (%)	actual (g)	corr. (g)	in A (%)	in Ts (%)	(g)	in A (%)	in Ts (%)
AS-1	1865.0	18.6	20.1	1.00	0.92	1833.7	1834.3	98.35	90.87	10.6	0.65	0.61
AS-2	1118.9	43.5	43.8	3.80	3.61	1068.2	1068.4	95.39	90.72	6.7	0.81	0.77

TABLE 8

Fractionation of the Aromatics BS-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% in TsS-1)
Taken for fractionation		17.1	1.4946	0.8610	
I	78.7-100.0	0.7	1.4788	0.8431	0.04
II	100.0-127.2	3.5	1.4909	0.8548	0.18
III	127.2-145.7	11.35	1.4957	0.8639	0.61
Residue		0.3	—	—	0.02
Losses		1.25	—	—	0.07

Results of the Optical Analysis of Fraction III:

Amt. in TsS-1 (% by wt.)

o-Xylene	5%	0.03
m-Xylene	30%	0.18
p-Xylene	20%	0.12
Ethylbenzene	45%	0.28

TABLE 9

Fractionation of the Aromatics BS-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% in TsS-2)
Taken for fractionation		41.4	1.4979	0.8675	
I	77.7 - 101.2	9.8	1.4998	0.8742	0.88
II	101.2 - 127.2	11.15	1.4971	0.8660	1.00
III	127.2 - 145.3	17.9	1.4980	0.8664	1.61
Residue		0.55	—	—	0.05
Losses		3.0	—	—	0.07

Results of the Optical Analysis of Fraction III are given on page 231.

Results of the Optical Analysis of Fraction III

Amt. in TsS-2
(% by wt.)

o-Xylene	20%	0.32
m-Xylene	37%	0.59
p-Xylene	16%	0.25
Ethylbenzene	27%	0.45

Dehydrogenation over platinized charcoal

containing iron yielded the catalyzates D, which had the following properties: GS-1 - n_D^{20} 1.4410; d_4^{20} 0.7836; aniline point 12.9°; GS-2 - n_D^{20} 1.4240; d_4^{20} 0.7519; aniline point 35.5°.

Separation of the Catalyzates D into Aromatic Hydrocarbons and a Mixture of Paraffins and Cyclopentanes. The D fractions were subjected to chromatographic separation on silica gel. This resulted in the separation of the aromatics (E), formed by the dehydrogenation of cyclohexane hydrocarbons, and the paraffin-cyclopentane part (F). The results of the separation are given for the two gasolines in Table 11.

TABLE 11

Chromatographic Separation of the Catalyzates GS-1 and GS-2

Fraction	Amt. of catalyzates taken (g)	Results of separation					
		Aromatics (E)		Paraffin-cyclopentane part (F)		Losses	
		(g)	(% in D)	(g)	(% in D)	(g)	(% in D)
GS-1	677.0	300.0	44.31	373.0	55.10	4.0	0.59
GS-2	679.0	200.5	29.53	470.5	69.29	8.0	1.18

TABLE 12

Fractionation of the Aromatics DS-1

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}
Taken for fractionation		69.6	1.4964	0.8642
I	79.0 - 101.9	12.55	1.4992	0.8751
II	101.9 - 127.1	34.35	1.4962	0.8654
III	127.1 - 146.1	17.6	1.4971	0.8650
Residue		4.4		
Losses		0.8		

Results of the Optical Analysis of Fraction III

o-Xylene	11%
m-Xylene	56%
p-Xylene	11%
Ethylbenzene	22%

TABLE 10

Amounts of the Fractions Taken and Obtained in the Dehydrogenation of BS-2 Aromatics

Fraction	Amt. taken	Amt. of D obtained (g)	
		Actual	Corr.
BS -1	742	699.0	699.5
BS -2	728	698.0	698.2

TABLE 13

Fractionation of the Aromatics DS-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	n_D^{20}	d_4^{20}
Taken for fractionation		67.15	1.4960	0.8654
I	78.2 - 100.5	11.1	1.4972	0.8715
II	100.5 - 127.9	30.75	1.4948	0.8629
III	127.9 - 148.8	23.5	1.4967	0.8655
Residue		1.75		
Losses		0.05		

Results of the Optical Analysis of Fraction III

o-Xylene	23%
m-Xylene	35%
p-Xylene	18%
Ethylbenzene	24%

Owing to the high content of aromatics in the D catalyzates, their separation on silica gel was effected with the aid of a displacing liquid, isopentane. There was therefore no need to consume any of the investigated mixture of hydrocarbons in the refractive index determinations and formolite tests. The actually separated amounts of E and F, which are given in Table 11, were therefore used in the calculations.

Investigation of the Aromatics (E). The chromatographically separated aromatic hydrocarbons E were fractionated through a 40-plate column. Simultaneously fractionation curves were determined and fractions were collected corresponding to benzene, toluene, and the xylenes. The xylene fractions were investigated optically.

The results of the fractionations, the properties of the fractions, and the results of the optical analysis are given in Tables 12 and 13. The fractionation curve for DS-1 is given in Fig. 3.

Since the aromatic hydrocarbons E were obtained as a result of the dehydrogenation of the cyclohexane

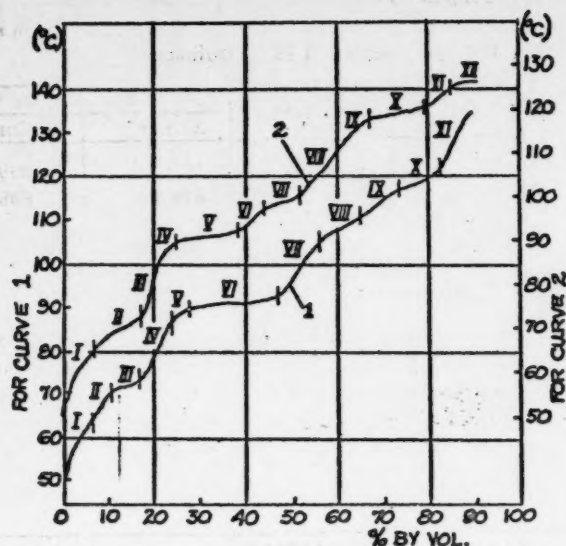


Fig. 4. Fractionation curves for the fractions ES-1 (1) and ES-2 (2).

TABLE 14
Fractionation of the Paraffin-Cyclopentane Part of ES-1

Fraction No.	Boiling range (°C at 760 mm)	Weight of fraction (g)	Amt. of fraction in TsS-1 (% by wt.)	n_D^{20}	d_4^{20}	Aniline point (°C)
Taken for fractionation		217.1	47.20*	1.4047	0.7277	58.0
I	44.5 - 63.0	10.9	2.37	1.3735	0.6581	70.8
II	63.0 - 71.0	8.5	1.85	1.3822	0.6784	61.8
III	71.0 - 73.0	15.8	3.43	1.4052	0.7356	37.9
IV	73.0 - 86.5	13.0	2.83	1.3981	0.7048	56.2
V	86.5 - 90.0	8.8	1.91	1.4008	0.7206	58.1
VI	90.0 - 92.2	44.0	9.57	1.4032	0.7275	55.3
VII	92.2 - 105.0	17.2	3.74	1.4095	0.7409	51.1
VIII	105.0 - 111.0	22.7	4.93	1.4073	0.7346	62.3
IX	111.0 - 117.0	17.1	3.72	1.4073	0.7314	64.3
X	117.0 - 121.5	22.7	4.93	1.4117	0.7414	60.4
XI	121.5 - 133.0	9.8	2.13	1.4169	0.7542	59.0
XII	133.0 - 137.3	12.6	2.74	1.4172	0.7514	65.2
Residue		11.5	2.50	—	—	—
Losses		2.5	0.54	—	—	—

Tables 14, 15, 16, and 17 show the results of the fractionations, the physical properties, and the results of optical analysis. On the basis of these results the contents of paraffin and cyclopentane hydrocarbons in the whole gasolines were calculated.

The following took part in this investigation: senior laboratory assistant A. D. Matveeva and the laboratory assistants M. F. Zulina, T. V. Lapshina, V. A. Ovodova, K. G. Ryabova, and G. S. Taits.

SUMMARY

1. With the aid of the combination method for the investigation of the individual hydrocarbon composition

* Here and in Table 16 the amount indicated is the percent content in TsS-1 and in TsS-2 of the whole of the given fraction, and not for the portion taken for investigation.

hydrocarbons present in the gasoline, the benzene fractions of the aromatics E correspond to cyclohexane, the toluene fractions to methylcyclohexane, and the xylene fractions to dimethyl- and ethyl-cyclohexanes. From the results obtained relating to the amount and composition of the fractions of the aromatics E, taking into account the hydrogen removed in the dehydrogenation, the contents of the cyclohexane hydrocarbons in the gasolines were calculated.

The results of the calculation are given in Table 2, in which the results are summarized.

Investigation of the Paraffin-Cyclopentane Fractions (F). The paraffin-cyclopentane parts F, left after separation of the aromatics E by chromatographic adsorption, were fractionated through a 50-plate column. As a preliminary, the fractionation curve was determined for 100 ml of the F fraction of each gasoline (ES-1 and ES-2), the results being shown in Fig. 4. The vertical lines on the curves indicate the cuts.

The fractions obtained were characterized by their physical properties and analyzed with the aid of Raman spectra.

TABLE 15

Results of the Optical Investigation of the Narrow Fractions of the Paraffin-Cyclopentane Part of ES-1

Hydrocarbons found by the optical method	Content (% by wt.)		Hydrocarbons found by the optical method	Content (% by wt.)	
	in the fraction	in TsS-1		in the fraction	in TsS-1
Fraction I			Fraction VII		
2,3-Dimethylbutane	45	1.07	cis- and trans-1,2-Dimethylcyclopentanes	70	2.62
2-Methylpentane	45	1.07	Heptane	Qualitatively	
2,2-Dimethylbutane	5	0.12	Ethylcyclopentane		
3-Methylpentane	Qualitatively		Methylcyclohexane		
Cyclopentane			Mixture of isomers of 1,3-dimethylcyclopentane		
Fraction II			Fraction VIII		
2-Methylpentane	65	0.60	1,2,4-Trimethylcyclopentane	70	3.45
3-Methylpentane		0.60	2,2-Dimethylhexane	10	0.49
Hexane	15	0.28	2,4-Dimethylhexane	10	0.49
Methylcyclopentane	20	0.37	2,5-Dimethylhexane	10	0.49
Fraction III			Fraction IX		
Methylcyclopentane	90	3.09	1 ^C , 2 ^t , 3 ^C -Trimethylcyclopentane	55	2.05
Hexane	10	0.34	2,3-Dimethylhexane	Qualitatively	
Fraction IV			Fraction X		
Methylcyclopentane	40	1.13	1,1-Dimethylcyclohexane	50	2.46
2,4-Dimethylpentane	40	1.13	2-Methylheptane	Qualitatively	
2,2-Dimethylpentane	Approx. equal	0.28	3-Methylheptane		
2,2,3-Trimethylbutane		0.28	4-Methylheptane		
3,3-Dimethylpentane	Qualitatively		Fraction XI		
Fraction V			1,1-Dimethylcyclohexane	25	0.53
1,1-Dimethylcyclopentane	50	0.86	Fraction XII		
3,3-Dimethylpentane	35	0.68	Not investigated optically		
2-Methylhexane	15	0.29			
Fraction VI					
trans-1,2-Dimethylcyclopentane	30	2.87			
cis- and trans-1,3-Dimethylcyclopentanes	20	1.91			
2-Methylhexane	30	2.87			
3-Methylhexane	20	1.91			

of gasolines, two gasoline samples, from first-grade and oil grade Surakhan petroleum respectively, have been analyzed.

2. The individual composition of the gasoline derived from first grade Surakhan petroleum has been accounted for quantitatively to the extent of 77.8%, and the gasoline from the oil-grade petroleum has been accounted for to the extent of 84.0%. Altogether, 47 hydrocarbons have been determined quantitatively in the two gasolines.

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- [1] G. S. Landsberg and B. A. Kazansky, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1951, No. 2, 100.
 [2] B. A. Kazansky, A. F. Plate, E. A. Mikhailova, A. L. Liberman, M. I. Batuev, T. F. Bulanova, and G. A. Tarasova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1954, No. 2, 266.*

* See Consultants Bureau Translation, page 215.

TABLE 16

Fractionation of the Paraffin-Cyclopentane Part of ES-2

Fraction No.	Boiling range (°C at 760 mm)	Wt. of fraction (g)	Amt. of fraction in TsS-2 (% by wt)	n_D^{20}	d_4^{20}	Ani-line point (°C)
Taken for fractionation		213.5	60.3	1.3990	0.7132	62.8
I	43.0 - 65.0	13.5	3.81	1.3762	0.6758	66.8
II	65.0 - 72.2	20.8	5.88	1.3855	0.6858	57.7
III	72.2 - 83.5	7.7	2.17	1.4026	0.7289	44.6
IV	83.5 - 90.0	5.8	11.64	1.3962	0.7095	61.6
V	90.0 - 92.2	35.5	0.03	1.3979	0.7133	60.4
VI	92.2 - 97.0	5.4	1.53	1.3970	0.7094	61.2
VII	97.0 - 100.0	19.4	5.48	1.3906	0.6916	66.7
VIII	100.0 - 109.5	14.0	3.95	1.4063	0.7327	57.6
IX	109.5 - 117.5	18.3	5.17	1.4061	0.7292	64.9
X	117.5 - 120.0	25.8	7.29	1.4034	0.7197	67.4
XI	120.0 - 124.0	9.1	2.57	1.4097	0.7360	65.0
XII	124.0 - 127.0	14.7	4.15	1.4019	0.7156	68.1
XIII	127.0 - 136.3	9.3	2.63	1.4124	0.7408	65.8
Residue		11.0	3.10	1.4165	—	—
Losses		3.2	0.90	—	—	—

TABLE 17

Results of the Optical Investigation of the Narrow Fractions of the Paraffin-Cyclopentane Part of ES-2

Hydrocarbons found by the optical method	Content (% by wt.)	
	in the fraction	in TsS-2
Fraction I		
2-Methylpentane	65	2.48
3-Methylpentane		
Cyclopentane	20	0.76
2,3-Dimethylbutane	10	0.38
2,2-Dimethylbutane	5	0.19
Fraction II		
Methylcyclopentane	25	1.47
Hexane	65	3.82
3-Methylpentane	10	0.59
Fraction III		
Methylcyclopentane	65	1.41
2,2-Dimethylpentane	10	0.22
2,2,3-Trimethylbutane	5	0.11
2,4-Dimethylpentane	20	0.43
Fraction IV		
Not investigated optically		

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TABLE 17 -- (continued)

Hydrocarbons found by the optical method	Content (% by wt.)	
	in the fraction	in TsS-2
Fraction V		
2-Methylhexane	30	3.01
3-Methylhexane	20	2.01
1,3-Dimethylcyclopentane	20	2.00
trans-1,2-Dimethylcyclopentane	30	3.01
Fraction VI		
Not investigated optically		
Fraction VII		
Heptane	95	5.21
Not accounted for	5	0.27
Fraction VIII		
Heptane	30	1.19
Ethylcyclopentane	10	0.39
1,2,4-Trimethylcyclopentane	30	1.18
2,4-Dimethylhexane	10	0.39
Not accounted for	20	0.80
Fraction IX		
1,2,4-Trimethylcyclopentane	60	3.10
2-Methylheptane	30	1.55
Not accounted for	10	0.52
Fraction X		
2-Methylheptane	50	3.64
3-Methylheptane	40	2.92
1,1-Dimethylcyclohexane	10	0.73
Fraction XI		
2-Methylheptane	20	0.51
Octane	40	1.03
3-Methylheptane	30	0.77
1,1-Dimethylcyclohexane	10	0.26
Fraction XII		
Octane	95	3.94
1,1-Dimethylcyclohexane	5	0.21
Fraction XIII		
Octane	30	0.79
Propylcyclopentane	30	0.79
Isopropylcyclopentane	20	0.53
1,1,3 Trimethylcyclohexane	20	0.52

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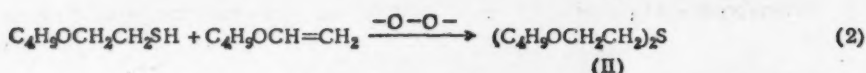
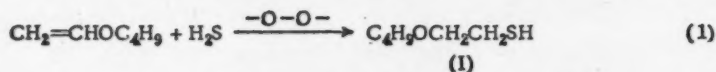
SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 7. PECULIARITIES OF THE REACTION OF ADDITION, CONTRARY TO MARKOVNIKOV'S RULE, OF HYDROGEN SULFIDE TO BUTYL VINYL ETHER

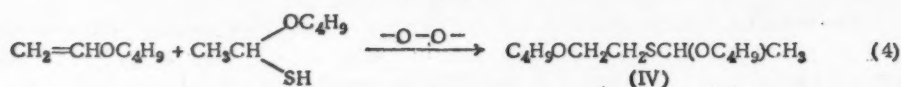
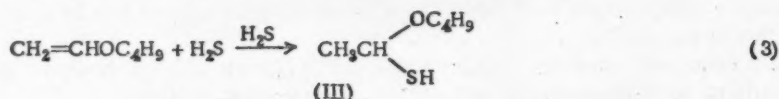
M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

When thiols react with vinyl ethers in sealed evacuated tubes, the addition reaction proceeds entirely in the direction contrary to Markovnikov's rule [1]. We have previously suggested [1] that in this case slight traces of oxygen act as catalyst, and that the reaction is a free-radical process, as in other cases of "anomalous" addition.

In the present investigation it has been shown that, when liquid hydrogen sulfide and butyl vinyl ether react under these conditions, the main products are 2-butoxyethanethiol (I) and bis(2-butoxyethyl) sulfide (II). By variation in the proportions of the ether and hydrogen sulfide, the reaction may be adjusted so as to give preferential formation of thiol or of sulfide, so that it is possible to synthesize either of these substances in fairly high yield:



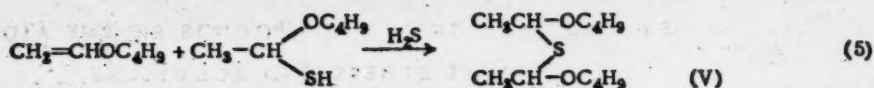
The sulfide fraction, however, always contains some of the isomeric 1-butoxyethyl-2-butoxyethyl sulfide (IV), the amount of which increases with increase in the initial concentration of hydrogen sulfide. As we have already shown experimentally [1] that under the conditions of the experiment thiols add to vinyl ethers exclusively in violation of Markovnikov's rule, the source of the sulfide IV can only be addition of hydrogen sulfide to the vinyl ether in accordance with Markovnikov's rule, resulting in the formation of 1-butoxyethanethiol (III, Equation 3), which, owing to its high reactivity, will rapidly react "anomalously" with the ether (Equation 4):



A knowledge of the amount of the sulfide IV formed, therefore, will enable us to calculate the proportion of the hydrogen sulfide molecules reacting in accordance with Markovnikov's rule. As will be seen from the results shown in Table 1 (Experimental Part), in the majority of the experiments it did not exceed 10%. Hence, in spite of statements in the literature [2], under mild conditions hydrogen sulfide may add to an ethylene bond mainly in the direction contrary to Markovnikov's rule (in presence of the catalysts that bring about the addition of thiols).

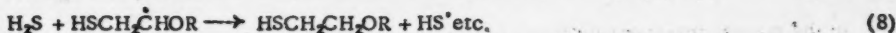
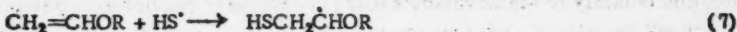
In the Experimental Part of this paper we show quite definitely that, as stated previously, the catalyst operative under these conditions consists of traces of oxygen dissolved in the vinyl ether. Direct proof of this is furnished by the considerable acceleration of the reaction induced by introduction into the tube of a quantity of dry oxygen, not exceeding 0.01% by weight (Table 3). The principal indirect proofs are: 1) the considerable reduction in the reaction rate, without effect on its direction, resulting from repeated distillation of the vinyl ether in a current of nitrogen before the experiment; 2) the complete inhibition of the reaction of anomalous addition in presence of the antioxidant hydroquinone, added in an amount of about 0.5% on the weight of the ether (Table 2). In presence of the antioxidant, addition to butyl vinyl ether in accordance with Markovnikov's rule is to be observed, and this

occurs not only with hydrogen sulfide (Equation 3), but also with the thiol formed (Equation 5), evidence for this reaction being provided by the appearance of bis(1-butoxyethyl) sulfide (V) in the reaction mixture.

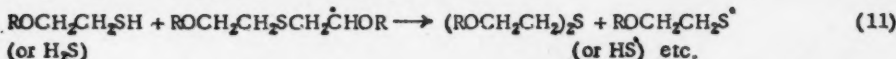
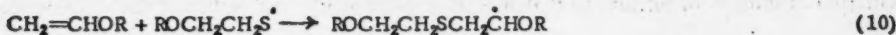
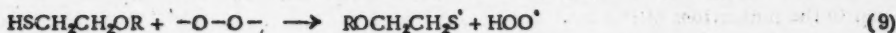


Traces of oxygen, therefore, served as catalyst for "anomalous" addition. As will be shown below, the products of the oxidation of the vinyl ether have just the opposite effect on the reaction, and can therefore certainly not catalyze it.

The mechanism of "anomalous" addition may be represented by the usual scheme for a chain free-radical process [3]:



and further



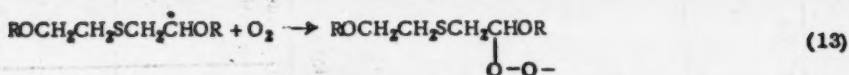
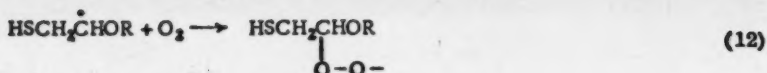
The stages 6 - 8 (addition of hydrogen sulfide) are somewhat more rapid than the stages 9 and 10 (addition of thiol), since 2-butoxyethanethiol is almost always present in the reaction medium.

The free-radical addition reaction between hydrogen sulfide and butyl vinyl ether is distinguished by a number of peculiarities that cannot in any way be reconciled with Kharash's peroxide theory, and in this respect we again meet the situation found in the addition reaction between thiols and vinyl ethers that we studied previously [1]. Thus, we have established (Table 4), that oxidation products, formed by long storage of the ether in contact with the air, and also benzoyl peroxide and hydrogen peroxide, not only do not accelerate anomalous addition, but in fact, considerably retard it, which leads (depending on the initial concentration of hydrogen sulfide) either to complete inhibition of the process, or to addition of the residues of the sulfur compounds in accordance with Markovnikov's rule. It was found that suitable catalysts for anomalous addition were ascaridol (Table 6) and small amounts (about 0.1% by weight) of a concentrated solution of hydrogen chloride in dioxane, which contains a peroxide of unknown structure [4] (Table 5). This reaction, therefore, is characterized by specificity in its requirements with respect to the peroxide catalyst.

The behavior of this reaction toward molecular oxygen is very peculiar. Although slight traces of dissolved oxygen constitute a positive catalyst for the process of "anomalous" addition, its introduction into the reaction medium even in amounts of about 0.05% by weight has a marked inhibiting effect, and leads, as in the case of benzoyl peroxide and hydrogen peroxide, to the predominant formation of products in accordance with Markovnikov's rule (Table 3). Approximately the same amounts of oxygen, however, have been used by some authors [5] for the acceleration of the anomalous addition of HBr to allyl bromide, and no retarding effect was observed in this system of reactants. We may recall that Kharash and coworkers early suggested that peroxides and oxygen act exclusively as catalysts in anomalous addition reactions.

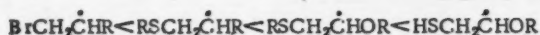
Our experiments show that the Kharash peroxide theory in its existing form is not valid in all liquid-phase addition reactions having a free-radical mechanism. Peroxides or oxygen are not always catalysts for free-radical addition reactions; their catalytic activity for certain systems is very specific, and evidently depends on the energy of formation, and therefore the method of formation, of the radical initiating the chain (in our case RS^\bullet , formed by Equations 6 and 9).

The chemical nature of the radical propagating the chain (in our case $\text{RSCH}_2\dot{\text{C}}\text{HOR}$) is of particular importance for the further course of the reaction, mainly with respect to its tendency to undergo oxidation or reduction reactions. From our point of view, the inhibiting effect of appreciable amounts of oxygen, and also of H_2O_2 and benzoyl peroxide, is to be associated with termination of chains due to ready oxidation, in accordance with Equations 12 and 13, of the radicals formed by Equations 7 and 10:



Such oxidation inhibits the formation of the end products and the regeneration of the original radicals in accordance with Equations 8 and 11, and it may result finally in the accumulation in the reaction medium of oxidized substances of the type obtained by Mikhallov and Blokhina [6], and also by Kharash [7] in the simultaneous action of thiols and oxygen on olefins. In the case of vinyl ethers these oxidation products will be acidic in character and may even be catalysts for the addition of sulfur compounds in accordance with Markovnikov's rule. A supposition of this kind regarding the part played by oxygen is made all the more probable by the fact that its inhibiting effect is well known in polymerization reactions [8] and gas-phase reactions in which halogens [9] and HBr [10] add at a double bond, and is explained in the same way.

The retarding of the addition reaction by excess of oxygen or of a peroxide should be directly related to the tendency of the radical propagating the chain to undergo further oxidation. The existing experimental data indicate that the radicals in certain liquid-phase addition reactions may be arranged in the following series of increasing tendency to undergo oxidation:



Actually, no inhibiting effect due to peroxides or oxygen has been noted in the addition reactions between hydrogen bromide and olefins. There is only one reference to inhibition by peroxides of the liquid-phase addition reaction between thiols and olefins [11]. Finally, among the reactions of vinyl ethers, the inhibiting effect of oxygen is particularly marked for the addition of H_2S , and somewhat less marked for the additions of thiols [11].

In order to bring existing theory into accord with the new experimental facts, it is essential to make a more detailed study of the chemical nature of the radicals formed in addition reactions. Also, at the present stage of investigation, the general and indiscriminate approach to the mechanism of the action of oxidative chain catalysts that is characteristic of Kharash's peroxide theory is quite inadequate.

EXPERIMENTAL

For most of the experiments butyl vinyl ether was purified by the standard method described in detail in a previous communication [1]. The HCl-dioxane catalyst was prepared as described previously [4], and according to titration, it contained 25-27% of HCl. The ascaridol used was almost 100% in strength, and was prepared by a method given in the literature [12] from Soviet chenopodium oil. The method used for the titration of the mixture of sulfides, based on the decomposition of the 1,2'- and 1,1'- isomers in presence of excess of an alcoholic solution of mercuric chloride, has also been described by us previously [4]. In the last column of the tables we give the percentage of the H_2S molecules that add in accordance with Markovnikov's rule (referred to briefly as "a-addition of H_2S "). This is calculated, on the basis of the considerations given in the introduction to this paper, by multiplication of the content of the 1,2'-isomer (% 1,2') in the mixture of sulfides, as found by titration, by the yield of the sulfide fraction (% sulf. fr.)/100:

$$\text{a-Addition of } \text{H}_2\text{S} (\%) = \frac{(\% 1,2') (\% \text{ sulf. fr.})}{100}$$

In most of the experiments the procedure was as follows. A weighed sample of the ether was placed in a tared tube having a constriction. With the aid of a cap having an exit tube and a capillary for the introduction of gas, the air was displaced from the tube by a current of dry hydrogen sulfide from a Kipp's apparatus, after which the lower end of the tube was immersed in liquid nitrogen in a Dewar vessel in order to liquefy the required amount of hydrogen sulfide. In the course of this operation the current of hydrogen sulfide and the cooling were regulated in such a way that a feeble current of excess gas was always passing through the bubbler at the exit, thus making sure that no oxygen or moisture could find its way into the system from the atmosphere. When the necessary increase in weight was attained, the cap was replaced by a rubber tube attached to a tap, and the reaction tube was again cooled in liquid nitrogen (with the tap closed), and was then attached to a vacuum pump and evacuated down to 4-7 mm; after 20-30 minutes the constriction was sealed off while pumping continued. When it was intended that the synthesis of thiol should predominate and the tube contained a large excess of hydrogen sulfide, it was transferred in the chilled condition to the autoclave, into which nitrogen was passed from a cylinder up to a

TABLE 1

Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Absence of Specially Added Catalysts

Expt. No.	Amount taken		Experimental conditions		Unchanged ether (g)	Yield of reaction products		Amount of 1,2'-isomer in sulfide fr. (%)	α -Addition of H ₂ S (%)
	ether (g)	H ₂ S (moles per mole of ether)	total duration (days)	temperature (°C)		thiol (on ether)	total yield on ether		
22	20	0.5	1	-	19.5	-	-	-	-
96	20.6	0.49	1.5	-	18.9	-	<10	-	-
90	20.5	0.47	5	-	9.0	37.0	92.0	5.5	~3
52	25	0.4	10	-	14.5	40.4	96.3	7.4	~4
91	20.3	0.48	13	-	7.2	27.7	90.4	2.5	~2
54	25	0.85	10	-	7.8	55.4	90.2	17.2	~6
47	25	0.4	5	60	6.4	6.8	94.5	1	~1
14	30	1.0	7	60	-	52.6	96.0	20.0	~9
46	25	1.2	4	60	1.1	56.1	92.9	18.5	~7

TABLE 2

Effect of Antioxidants and the Conditions of the Purification of the Starting Materials on the Reaction Between Liquid Hydrogen Sulfide and Butyl Vinyl Ether

Expt. No.	Amt. of H ₂ S (moles per mole of ether)	Experimental conditions			Unchanged ether (%)	Yield of reaction products (%)			Amt. of 1,2'-isomer in sulfide fr. (%)	α -Addition of H ₂ S (%)
		total duration (days)	temperature (°C)	duration of heating (hr)		thiol (on ether)	sulfide (on ether)	total yield on ether		
47	0.38	5	60	30	Standard	6.8	87.7	94.5	97.0	~1
38	0.31	3	75	17	Preliminary fractionation of H ₂ S through a Davis column [13]	11.3	78.3	89.4	86.7	~1
31	0.38	7	75	21	Ether distilled twice in a current of nitrogen	-	90.1	90.1	62.1	~1.5
57	0.37	7	60	36	Ether kept for 11 days over hydroquinone; distilled off on the day of the experiment (in the air)	7.8	84.5	91.3	90.9	~4
53	0.42	7	60	30	Hydroquinone (0.01 g) introduced into the tube	14.5	78.0	92.5	88.4	~6
49	0.39	4	60	30	Hydroquinone (0.1 g) introduced into the tube	50.0	-	50.0	9.0	-
46	1.2	4	60	30	Standard conditions	56.1	36.8	92.9	-	~7
56	1.2	7	60	36	Ether as in Expt. No. 57	60.7	34.2	94.9	-	~7
48	1.2	6	60	30	Hydroquinone (0.1 g) introduced into the tube	31.5	60.0	91.5	-	(above 60%)

* Since the mixture of sulfides obtained in this experiment consisted of three isomers, the exact determination of the proportions by titration was impossible. This note applies also to all analogous cases given in the succeeding tables.

TABLE 3

Effect of Oxygen on the Addition of H₂S to Butyl Vinyl Ether (All experiments were carried out at room temperature with 20-25 g samples of ether)

Expt. No.	Amount taken H ₂ S (moles per mole of ether)	Duration of expt. (days)	Unchanged ether (%)	Yield of reaction products (%)			Amount of 1,2'-isomer in sulfide fr. (%)	Nature of thiol fraction	α -Addition of H ₂ S (%)
				thiol (on ether)	sulfide (on ether)	total yield (on ether)			
96	0.49	1.6	94	—	—	—	—	β	~ 1
90	0.47	5	45	37.0	55.0	92.0	6.5	β	~ 3
91	0.48	13	35	27.7	62.7	90.4	2.5	β	~ 1.5
80	1.4	13	4	30.6	63.3	93.9	138	$\alpha + \beta$	~ 100
81	0.38	13	27	12.5	80.7	93.2	129	$\alpha + \beta$	~ 100
82	1.3	13	22	40.4	33.1	73.2	59.7	$\beta + \alpha$	~ 20
83	0.44	13	50	33.6	47.0	80.6	48.8	$\beta + \alpha$	~ 20
105	0.43	1.6	48	39.3	47.0	86.3	3.1	β	~ 1.5
98	0.45	6	34	33.7	55.3	89.0	5.8	β	~ 3

TABLE 4

Retarding Effect of the Oxidation Products of the Vinyl Ether and of Certain Peroxides on the Addition of H₂S Contrary to Markovnikov's Rule

Expt. No.	Amt. of H ₂ S (moles per mole of ether)	Experimental conditions				Unchanged ether (%)	Yield of reaction products (%)		Amt. of 1,2'-isomer in sulfide fr. (%)	α -Addition of H ₂ S (%)
		total duration (days)	temperature (°C)	duration of heat (hr)	method of purification of ether; added peroxides		thiol (on ether)	sulfide (on ether)		
47	0.38	5	60	30	Standard	25.6	16.8	87.7	97	1
91	0.48	13	—	—	Standard	35.4	24.7	62.7	80.0	2.5
66	0.36	4	60	30	Ether kept for a long time over potassium carbonate	44.4	35.9	52.8	94.4	3.2
63	0.42	6	60	30	Ether kept for 36 days over sodium	53.2	42.6	43.1	85.7	7.4
62	0.42	5	60	30	Ether kept for 80 days over sodium	48.0	45.8	30.2	79.0	12.0
70	0.37	6	60	32	Benzoyl peroxide (0.02 g) introduced into the tube	68.5	27.1	70.4	52.5	62.2
60	0.36	12	—	—	Benzoyl peroxide (0.2 g) introduced into the tube	84	19.6	54.4	74.0	89.6
92	0.47	13	—	—	Hydrogen peroxide (27%, 0.2 ml) introduced into the tube	9.5	32.1	21.8	53.9	190
17	0.63	8	70	30	Water (0.2 ml) introduced into the tube	3	24.6	73.9	—	8

pressure of 15-16 atm so as to equalize pressures inside and out. After the reaction the tube was transferred with all necessary precautions from the autoclave to a Dewar flask containing liquid nitrogen, and was then opened in the chilled condition. The excess of hydrogen sulfide was evaporated off, and the reaction products were vacuum-fractionated.

When it was intended that the synthesis of sulfides should predominate, the reaction tube was placed in a closed metal tube and, in a number of experiments, was heated in a water thermostat for the necessary time. Breakage of the tube occurred only rarely, and was generally associated with bad sealing. Although practically the whole of the hydrogen sulfide was consumed by the end of the reaction in these experiments, the precaution was taken to open the tubes in the chilled condition. When the reaction products were fractionated, unchanged vinyl ether was trapped in a cooled coil, and the thiol and sulfide fractions were then collected. The sulfide fraction was titrated with 0.1 N NaOH after addition of mercuric chloride, as described previously [4]. When the experiments were carried out in presence of catalysts or other substances, these were dissolved beforehand in the ether, or were added directly to the tube.

In the accompanying tables the yields of reaction products are expressed in terms of the amount of ether that reacted, not the amount taken. The overall yield of products, therefore, does not give an indication of the extent to which the reaction proceeded, but shows the balance of products in the given experiment. The amount of unchanged ether is shown separately. In the experiments in which the amount of hydrogen sulfide taken was less than 0.5 mole per mole of the ether, the yield of products based on the amount of H_2S taken is also given, thus making it possible to obtain an idea of the extent to which it combines during the reaction.

1. Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Absence of Specially Added Catalysts (in Presence of Traces of Oxygen). The optimum conditions for the synthesis of bis(2-butoxyethyl) sulfide were found to require the use of excess of the ether (1 mole to 0.4 mole of H_2S) and the application of heat. For the synthesis of 2-butoxyethanethiol, an excess of H_2S (more than 1 mole per mole of the ether) was required and the reaction was carried out in the cold. Table 1 gives the results of experiments with ether samples weighing 20-30 g; for bigger samples the time required for reaction was naturally longer. For example, for the synthesis of the sulfide from 100 g of the ether, heating must be for 80-90, not 30 hours.

Example. Experiment No. 47 (Table 1). Fractionation yielded 6.4 g of unchanged ether and:

Fraction I, b.p. 40-43° (5 mm); n_D^{20} 1.4489; 1.7 g

Fraction II, b.p. 43-130° (5 mm); one or two drops

Fraction III, b.p. 130-132° (5 mm); n_D^{20} 1.4559; 19.1 g

Fraction I corresponded in boiling point and refractive index to 2-butoxyethanethiol, which we have synthesized previously [4]. With mercuric chloride it gave white crystals of the mercurichloride $C_4H_9OCH_2CH_2SHgCl$, m.p. 137.5-138° [4].

Analysis showed that Fraction III contained only about 1% of 1-butoxyethyl 2-butoxyethyl-sulfide, and its boiling point and refractive index corresponded to bis(2-butoxyethyl) sulfide $(C_4H_9OCH_2CH_2)_2S$, which we have synthesized previously [4]. Hence, under the conditions of the experiment, both hydrogen sulfide and 2-butoxyethanethiol added to butyl vinyl ether contrary to Markovnikov's rule.

2. Effect of Antioxidants and the Conditions of the Purification of the Starting Materials on the Reaction Between Liquid Hydrogen Sulfide and Butyl Vinyl Ether. Table 2 gives the results of comparative experiments having the object of determining the nature of the catalyst causing addition of hydrogen sulfide to butyl vinyl ether contrary to Markovnikov's rule. For comparison purposes, two standard experiments (No. 46 and 47) are given in which the reactants were purified in the usual way and no additions were made. In all of the experiments 25-30 g samples of the ether were used.

Prior distillation of the hydrogen sulfide (Expt. No. 38) did not have any essential effect on the character of the reaction and the reaction rate, and the addition catalyst, therefore, was not present as a contaminant in the hydrogen sulfide. In this experiment, distillation of the hydrogen sulfide was effected with the aid of a Davis column [13], the fraction of b.p. -60 to -59° being collected. The distilled hydrogen sulfide, which was collected in a cooled trap, was quickly evaporated and passed to the tube containing butyl vinyl ether, and the experiment was then carried out under standard conditions. Expt. No. 31 showed that distillation of the vinyl ether in a current of nitrogen, which reduced the amount of dissolved oxygen, considerably retarded the reaction (by a factor of two). Long treatment of the ether with hydroquinone followed by distillation on the day of the experiment (Expt. No. 57 and 56) had practically no effect on the character of the reaction (the distillation was performed not in a current of

TABLE 5

Addition of H₂S to Butyl Vinyl Ether Under the Catalytic Action of a Concentrated Solution of HCl in Dioxane (0.01 ml per 10 g of ether)

Expt. No.	Amount taken		Experimental conditions		Unchanged ether (g)	Yield of reaction products (%)			Amount of 1,2'-isomer in sulfide fr. (%)	α -Addition of H ₂ S (%)
	ether (g)	H ₂ S (moles per mole of ether)	total duration (days)	temperature (°C)	duration of heating (hr)	thiol (on ether)	sulfide (on ether)	total yield on ether on H ₂ S		
26	155	0.42	2	-	-	15.2	70.7	85.9	9	~ 6
6	70	0.43	3	-	-	11.0	79.0	90.0	4.2	~ 4
28	100	0.43	11	-	-	0.9	94.4	95.3	3.4	~ 3
7*	70	0.99	5	-	-	19.6	46.5	95.2	18.1	> 8
3*	40	1.35	1	70	8	54.3	36.8	91.1	31.8	> 11
16*	60	1.6	3	-	-	52.7	27.6	80.3	48	> 13
10*	60	2.0	2	-	-	68.2	19.1	87.3	40.7	> 8
15*	60	2.5	4	-	-	72.6	19.7	92.2	47	> 9
37**	24.3	0.45	6	60	26	-	78.3	78.3	47.6	~ 30
25***	19.2	0.53	1	-	-	-	80.0	80.0	72.8	~ 50

* In Expt. No. 7, 3, 16, 10, 15 the thiol fraction contained some 1-butoxyethanethiol, so that the α -addition of H₂S was actually somewhat higher than that calculated from the titration of the sulfide part.

** In this experiment 0.1 g of hydroquinone was introduced into the tube. Apart from a sulfide fraction containing all three isomers, decomposition products of these were obtained [4], namely 2,3 g of acetaldehyde dibutyl acetal and 1.5 g of acetaldehyde bis(2-butoxyethyl) mercaptal.

*** In this experiment the butyl vinyl ether used was first shaken for 27 hours in an atmosphere of dry oxygen. Here again 1.5 g of the acetal and 1.1 g of the mercaptal were obtained, and the sulfide fraction contained all three isomers.

TABLE 6

Addition of H₂S to Butyl Vinyl Ether Under the Catalytic Action of Ascaridol

Expt. No.	Amount taken		Experimental conditions		Unchanged ether (g)	Yield of reaction products (%)			Amount of 1,2'-isomer in sulfide fr. (%)	α -Addition of H ₂ S (%)
	ether (g)	H ₂ S (moles per mole of ether)	total duration (days)	temperature (°C)	duration of heating (hr)	thiol (on ether)	sulfide (on ether)	total yield on ether on H ₂ S		
77	60	1.55	6	-	-	63.4	33.1	94.5	7	~ 2
75	60	1.98	6	-	-	74.5	21.9	96.4	4	~ 1
74	60	2.03	6	-	-	69.0	24.1	93.1	1	~ 1
86	20	1.6	2	-	-	74.5	21.3	95.8	5	~ 1
101	20	2.13	2	-	-	77.0	13.8	90.8	1.5	~ 0.5
88	20	0.37	2	60	13.5	7.1	87.8	95.9	3.1	~ 2

nitrogen, but in the air); by this treatment the peroxide compounds in the ether itself were destroyed, but the amount of dissolved oxygen may have remained the same. Finally, in Expt. No. 53 the introduction of 0.01 g of hydroquinone (an amount insufficient to suppress the reaction) into the reaction medium somewhat increased the proportion of hydrogen sulfide molecules that added "normally", without effecting any essential change in the process as a whole. In Expt. No. 49 with a low concentration of hydrogen sulfide, the introduction of 0.1 g of hydroquinone practically stopped the reaction: during the standard time only 9% of the hydrogen sulfide reacted.

In Expt. No. 48 with a high concentration of hydrogen sulfide, the introduction of 0.1 g of hydroquinone resulted in the occurrence of addition mainly in the direction required by Markovnikov's rule. The thiol fraction consisted of a mixture of 1-butoxyethanethiol (1.1 g) and 2-butoxyethanethiol (7.4 g), and the sulfide fraction contained all three possible isomers. Titration showed that the content of bis(1-butoxyethyl) sulfide (V) (which yields two molecules of HCl in excess of a mercuric chloride solution [4]) in the sulfide fraction was not less than 16%, and that the total fraction of the hydrogen sulfide molecules that added in accordance with Markovnikov's rule was not less than 60%. The catalyst was in the nature of dissolved gas and appeared to be oxygen, since its action was paralyzed by the antioxidant hydroquinone.

3. Effect of Oxygen on the Addition of Hydrogen Sulfide to Butyl Vinyl Ether. Oxygen was passed from a graduated buret into the cooled tube, after it had been evacuated and immediately before it was sealed off. Expt. No. 105 and 98 (Table 3), when compared with the standard experiments, Expt. No. 96, 90, and 91, clearly demonstrate the catalytic acceleration of the reaction of anomalous addition of the sulfur-compound residues under the influence of small additions of oxygen, whereas Expt. No. 80-83 show the retarding effect of large additions of oxygen. In Expt. No. 80-83, the thiol fraction consisted of a mixture of 1- and 2-butoxyethanethiols, and the sulfide fraction consisted of a mixture of all three isomers, with a considerable predominance of *a*-addition products. In all experiments the yield of the thiol fraction was lower, and that of the sulfide fraction was higher, than in the standard experiments, behavior that is to be associated with the considerably higher reactivity of 1-butoxyethanethiol, as compared with its isomer. It will be quite clear that an excess of oxygen changes the direction of the reaction and increases its rate.

4. Retardation of the Anomalous Addition of Hydrogen Sulfide by Certain Peroxides. It will be seen from Expt. No. 62 and 63 (Table 4) that the ether, after prolonged standing over sodium (feeble peroxide reaction), gave rise to the following peculiarities: sulfide formation was considerably retarded, and the amount of the 1,2'-isomer in the sulfide fraction was increased. Ether that had been kept for a long time over potassium carbonate did not differ appreciably from the ether that had been given the standard purification (Expt. No. 66). Expt. No. 60, 70, and 92 showed that benzoyl peroxide and hydrogen peroxide produce a marked effect on the direction of the reaction: the yield of "normal" addition products was greatly increased, but, unlike oxygen, benzoyl peroxide caused a general retardation of the reaction. Expt. No. 17, which was carried out in presence of 0.2 ml of water, showed that water has no essential effect on the process, so that the effect produced by hydrogen peroxide could not have been due to the water present in this substance.

5. Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Presence of a Solution of HCl in Dioxane. A comparison of the results given in Table 5 with those in Table 1 shows that the introduction of the HCl-dioxane catalyst considerably accelerates the "anomalous" addition reaction, but increases the proportion of the hydrogen sulfide molecules that add in accordance with Markovnikov's rule to an insignificant extent. Expt. No. 37 shows that in this case some peroxide compound is acting as catalyst, for the introduction of hydroquinone, even at low hydrogen sulfide concentration, leads to a high yield of 1-butoxyethyl-2-butoxyethyl sulfide. In Expt. No. 25, the retardation of the "anomalous" reaction was brought about by peroxide compounds produced by agitation of the ether in an oxygen atmosphere for 27 hours. The HCl-dioxane catalyst accelerates the addition of H₂S to butyl vinyl ether, but it is particularly sensitive to oxygen and other contaminants, so that the results of the experiments are not always reproducible.

6. Addition of Hydrogen Sulfide to Butyl Vinyl Ether in Presence of Ascaridol. The most effective catalyst found for the anomalous addition of hydrogen sulfide to butyl vinyl ether was ascaridol. By the use of 0.1-0.13 g for each 10 g of the ether, we succeeded in accelerating this reaction considerably. The results of the experiments are given in Table 6.

SUMMARY

1. Methods have been developed for the synthesis of 2-butoxyethanethiol and bis(2-butoxyethyl) sulfide from butyl vinyl ether and hydrogen sulfide.

2. It has been shown that traces of oxygen (not more than 0.01% by weight), ascaridol, and the peroxide present in a concentrated solution of HCl in dioxane are catalysts for the addition of hydrogen sulfide to butyl vinyl ether contrary to Markovnikov's rule.

3. The free-radical nature of addition contrary to Markovnikov's rule is confirmed by the fact that it is retarded in presence of antioxidants.

4. It has been shown that a characteristic feature of the anomalous reaction is its inhibition by very small amounts of oxygen and peroxides, such as benzoyl peroxide, hydrogen peroxide, and the peroxide compounds formed during the storage of vinyl ethers.

5. It has been suggested that the inhibiting action of oxygen and peroxides is associated with the termination of chains resulting from the readily occurring secondary reaction in which radicals of the type $RSCH_2\dot{C}HOR$ (chain propagators) are oxidized.

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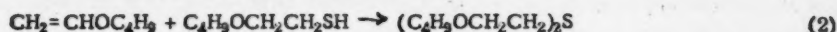
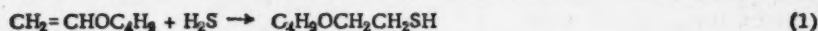
* See Consultants Bureau Translation, page 325.

SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 8. GENERAL METHOD FOR THE SYNTHESIS OF 2-ALKOXYETHANETHIOLS

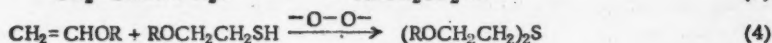
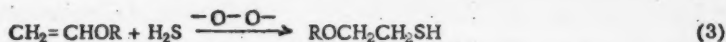
M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro

We have shown in the preceding communication [1] that, by the action of liquid hydrogen sulfide on butyl vinyl ether in presence of traces of oxygen from the air, it is possible to effect the addition of sulfur compounds to this ether in the direction contrary to that required by Markovnikov's rule, i.e., with formation of 2-butoxyethanethiol and bis(2-butoxyethyl) sulfide:

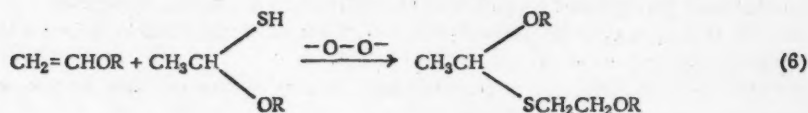
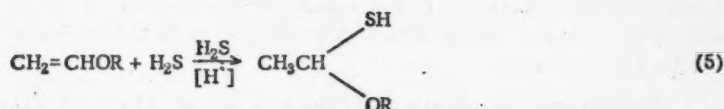


We have extended this reaction to the following vinyl ethers: ethyl, propyl, isopropyl, isobutyl, isopentyl, octyl, and cyclohexyl vinyl ether. On the basis of the products obtained in the reaction we may draw some tentative conclusions concerning the reactivities of vinyl ethers having radicals of different structure in the RO group.

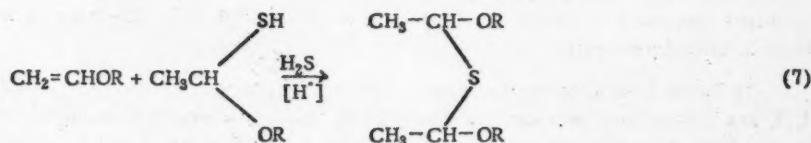
In general character, the reaction is the same for ethers in which R is an open-chain alkyl as for butyl vinyl ether. Thus, in most of the experiments the thiol fraction consisted almost entirely of 2-alkoxyethanethiol. The sulfide mixtures consisted of mixtures of the isomeric bis(2-alkoxyethyl) and 1-alkoxyethyl 2-alkoxyethyl sulfides in proportions that varied for different ethers, and only in exceptional cases did these mixtures contain any bis(1-alkoxyethyl) sulfide. Here, as in the case of butyl vinyl ether, it was found that as the initial hydrogen sulfide concentration was increased, there was an increase not only in the yield of thiol, but also in the yield of "normal" addition products. It may, therefore, be considered that the products of β -addition are formed by the overall reaction scheme expressed in Equations 3 and 4:



and having a free-radical chain mechanism. 1,2'-Products are formed by a process expressed by Equations 5 and 6, in which the first equation expresses the ionic addition of hydrogen sulfide to the vinyl ether, and the second represents the free-radical addition of the 1-alkoxyethanethiol formed:



Finally, 1,1'-dialkoxy sulfides are formed according to Equations 5 and 7 by reactions having an acid-catalyzed ionic character:



Comparison of the proportions of reaction products under comparable conditions may thus provide a measure of the higher or lower tendency of any one of the ethers to react with hydrogen sulfide by the free-radical (Equation 3) or ionic (Equation 4) reaction.

The overall rate of addition of hydrogen sulfide to the alkyl vinyl ethers fell greatly as the chain length increased. The vinyl ethers having normal radicals (ethyl, propyl, and octyl vinyl ethers) nevertheless gave mainly the products of addition occurring in violation of Markovnikov's rule. The presence of branching in the radical led to still slower reaction and also to considerable increase in the yield of "normal" addition products; this behavior apparently depends on the greater tendency of these ethers to undergo ionic reactions (isopropyl, and particularly isobutyl and isopentyl, vinyl ethers). It is characteristic that for these ethers the retardation of the free-radical addition under the influence of the oxidation products accumulating during long storage of the ethers in contact with air, which had already been observed for the case of butyl vinyl ether [1], was still more marked. Also, even for the most carefully purified samples of isopentyl vinyl ether, it was not found possible to accelerate this process appreciably at room temperature by addition of ascaridol, which was fairly effective in the case of butyl vinyl ether [1]. Thus, vinyl ethers having branched radicals undergo addition in the direction contrary to Markovnikov's rule only with great difficulty.

The behavior of cyclohexyl vinyl ether in this reaction was peculiar (Table 10). In presence of traces of oxygen the addition reaction proceeded extremely slowly, but the yield of "normal" addition products in the sulfide mixture was very high (60-90%). Introduction of the HCl-dioxane catalyst [1] greatly increased the rate of addition, but, at the same time, led to reduction in the yield of the primary products, as a result of secondary processes (with formation of cyclohexanol, the acetal, and the mercaptal). With respect to its behavior in this reaction, therefore, the cyclohexyl ether is to be associated with the ethers having branched radicals.

The reaction between any alkyl vinyl ether and hydrogen sulfide in molecular proportions of 1:2 results in the synthesis of the corresponding 2-alkoxyethanethiol in 55-80% yield. We have thus developed a simple general method of synthesis of 2-alkoxyethanethiols from vinyl ethers.

EXPERIMENTAL

All of the vinyl ethers used in this work were purified by the usual method [2]. In the purification of the ethers, all the precautions shown to be necessary in the preceding communication [1] were taken, and they then gave practically negative tests for peroxide with ferrocyanide [3]. The ethers had the physical constants cited in previous papers from this laboratory [2, 4, 5].

The method of carrying out the addition of hydrogen sulfide is described in the preceding communication [1]. The reaction products consisted of 2-alkoxyethanethiols and mixtures of isomeric dialkoxo diethyl sulfides. In the first fractionation of the reaction product, the thiol fraction came over within a narrow range of temperature and was readily separated, owing to the great difference in boiling point, from the sulfide fraction. The mixture of sulfides was analyzed for the content of 1,2'- and 1,1'-isomers by a method based on their decomposition in presence of excess of mercuric chloride (as previously described in detail [6]).

From the titration results we calculated the percentage of "normally" uniting hydrogen sulfide molecules, and these are indicated in Tables 4-10 as percent " α -addition of H_2S ". As in the preceding communication [1] we based the calculation on the fact that under the experimental conditions addition of thiols to vinyl ethers occurs, with rare exceptions, only in the direction contrary to Markovnikov's rule [7], so that " α -addition" products arise as a result of the "normal" reaction of hydrogen sulfide.

The pure bis(2-alkoxyethyl) sulfides were separated from the sulfide mixtures by a method in which the 1,2'-isomers were precipitated by means of an equimolecular amount of mercuric chloride [see the example of the purification of bis(2-propoxyethyl) sulfide]. The thiols were identified as mercurichlorides, and the sulfides as their complex salts with mercuric chloride. The physical properties and analyses of the substances synthesized are given in Tables 1-3. For the sake of completeness, these tables include also the 2-butoxy derivatives described in detail in previous communications [1, 6].

Of the mercury compounds given in Table 2, No. 1, 4, 5, and 6 were not analyzed, because their melting points were identical with those published by us previously, and no depression was given in mixture tests with the mercurichlorides previously synthesized by us by another method [6, 10]. The mercurichlorides No. 2, 3, 7, and 8 have not been described previously.

In Table 3 we give the properties of the bis(2-alkoxyethyl) sulfides synthesized; of these, the sulfides No. 1, 4, 5, and 6 have been previously prepared by us, and the constants given here coincide with those already published [6, 8, 10].* The constants given in the literature for sulfides No. 2 and 3 [11] are somewhat different from ours,

* We take this opportunity to correct regrettable misprints in previous communications [6], in which the boiling point of sulfide No. 1 was given incorrectly as 83.3-84.4° (3.5 mm), 83.8-84.4° (13.4 mm), instead of 83.8-84.4° (3.5 mm).

TABLE 1

No.	Formula	B.p. in °C (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR		Analysis					
					found	calculated	found			calculated		
							C	H	S	C	H	S
1	$C_2H_5OCH_2CH_2SH$	126-128 (760)	1.4456	0.9412	30.06	30.00	50.16	10.07	26.43	—	—	—
2	$n-C_3H_7OCH_2CH_2SH$	64 (40)	1.4478	0.9227	34.87	34.62	49.89	10.23	26.70	49.95	10.06	26.67
3	$iso-C_3H_7OCH_2CH_2SH$	56.1-56.4 (44)	1.4424	0.9186	34.84	34.62	50.19	10.22	26.40	49.95	10.06	26.67
4	$n-C_4H_9OCH_2CH_2SH$	48 (6)	1.4488	0.9111	39.50	39.24	50.17	10.10	26.44	—	—	—
5	$iso-C_4H_9OCH_2CH_2SH$	45.2-45.5 (9)	1.4444	0.9038	39.48	39.24	53.88	10.59	23.58	53.68	10.51	23.89
6	$iso-C_3H_7OCH_2CH_2SH$	53.9-54.5 (6)	1.4489	0.9028	44.01	43.86	57.07	11.11	21.56	56.70	10.88	21.66
7	$n-C_6H_{17}OCH_2CH_2SH$	103 (4.5)	1.4556	0.8906	58.05	57.71	57.30	11.06	21.74	63.41	11.65	16.83
8	$C_6H_{11}OCH_2CH_2SH$ (cyclohexyl)	73-73.5 (4.5)	1.4864	0.9938	46.33	46.28	63.10	11.87	16.85	60.06	10.12	20.15
							59.98	10.11	20.12	59.95	10.06	20.01

Note: The literature gives: for the thiol 1) b.p. 125.5-128°; d_4^{20} 0.9479 [8]; for the thiol 2) b.p. 48-50° at 17 mm [9]; and for the thiol 4) b.p. 167° [9]. The remaining thiols have not been described.

owing, probably, to the presence of impurities in the author's products. The complex salts of the sulfides No. 1, 2, 3, and 5 were of the composition $(ROCH_2CH_2)_2S \cdot HgCl_2$; they were not analyzed, for their melting points coincided with the values previously published by us [6, 10] and with values given in the literature [8, 11]. The complex salt of the sulfide No. 8 had the composition $(C_6H_{11}OCH_2CH_2)_2S \cdot 2HgCl_2$.

Found %: C 22.97;

23.09; H 4.03; 3.77; Cl 17.17; 17.27

$C_{16}H_{30}O_2S \cdot 2HgCl_2$. Calculated %: C 23.16;

H 3.65; Cl 17.09

The experiments on the addition of hydrogen sulfide to the individual ethers are summarized in Tables 4-10. The experiments for which no special indication is made were carried out without addition of catalyst, i.e., as we have shown previously, under the catalytic influence of traces of oxygen from the air. When a catalyst (HCl in dioxane [6] or ascaridol [1]) was used, it was always dissolved beforehand in the weighed sample of the ether. In all the tables the yields are calculated on the ether that reacted, not on the ether taken. For this reason, a separate indication is given in all tables of the amount of the vinyl ether recovered unchanged. Since the purification and separation of the reaction products were carried out similarly in all cases, detailed description has been confined to experiments on the addition of hydrogen sulfide to only two of the vinyl ethers (ethyl vinyl and propyl vinyl ethers).

I. Addition of Hydrogen Sulfide to Ethyl Vinyl Ether

The results of experiments on the addition of hydrogen sulfide to ethyl vinyl ether are given in Table 4. All of the experiments were carried out at room temperature. In Expt. No. 1, fractionation of the reaction products was carried out at atmospheric pressure and resulted in the partial decomposition of 1-ethoxyethyl 2-ethoxyethyl sulfide. In all of the remaining experiments the distillation was performed under reduced pressure.

Expt. No. 3. Ethyl vinyl ether (15.0 g) was placed in a tube having a constriction, and H_2S (9.7 g, i.e., 1.4 mole per mole of ether) was condensed in the tube as previously described [1]. The tube, while immersed in liquid nitrogen, was evacuated to a residual pressure of 4-5 mm (30 minutes), and sealed off while under vacuum. The tube was set aside for ten days at room temperature, and was then chilled in liquid

TABLE 2

No.	Formula	M.p. (in °C)	Analysis			
			found		calculated	
			C	H	C	H
1	$C_2H_5OCH_2CH_2SHgCl$	154.5-155.5	—	—	—	—
2	$n-C_3H_7OCH_2CH_2SHgCl$	137-137.5	17.06 17.04	3.23 3.27	16.90	3.12
3	$iso-C_3H_7OCH_2CH_2SHgCl$	153.5	16.83 16.63	3.28 3.33	16.90	3.12
4	$n-C_4H_9OCH_2CH_2SHgCl$	137.5-138	—	—	—	—
5	$iso-C_4H_9OCH_2CH_2SHgCl$	144-144.5	—	—	—	—
6	$iso-C_5H_{11}OCH_2CH_2SHgCl$	126	—	—	—	—
7	$n-C_2H_5OCH_2CH_2SHgCl$	126	28.28 28.28	4.81 5.01	28.24	4.98
8	$C_6H_{11}OCH_2CH_2SHgCl$ (cyclohexyl)	150.5	24.58 24.30	2.34 2.49	24.68	2.33

nitrogen and opened. Unchanged hydrogen sulfide was evaporated off. The increase in the weight of the reaction mixture resulting from bound (and, to some extent, dissolved) hydrogen sulfide was 5.4 g. Vacuum distillation yielded the following fractions:

Fraction I, b.p. 56-58° (60 mm); 13 g; n_D^{20} 1.4460

Fraction II, b.p. 58-100° (60 mm); 0.5 g

Fraction III, b.p. 91.5-92° (5 mm); 5.1 g; n_D^{20} 1.4556

After a second fractionation Fraction I came over completely at 126-128° (atmospheric pressure) and was found to be 2-ethoxyethanethiol, obtained in 58.9% yield (for constants see Table 1). The mercurichloride of this thiol melted at 154.5-155°.

After refractionation, Fraction III had b.p. 135-136° (50 mm); 83.8-84.4° (3.5 mm); 92.5-92.8° (6 mm); n_D^{20} 1.4555, i.e., constants very close to those of bis(2-ethoxyethyl) sulfide, previously synthesized by us [6], and also described in the literature [8, 11]. By titration with 0.1 N NaOH after addition of excess of mercuric chloride [6], the content of the isomeric 1-ethoxyethyl 2-ethoxyethyl sulfide in this fraction was found to be 7.7%. The yield of sulfide fraction was 27.5%.

Hence, under the experimental conditions used, ethyl vinyl ether reacts smoothly with hydrogen sulfide with formation mainly of addition products formed in violation of Markovnikov's rule.

II. Addition of Hydrogen Sulfide to Propyl Vinyl Ether

Results relating to the addition of hydrogen sulfide to propyl vinyl ether are given in Table 5.

Expt. No. 1. The experimental conditions are given in Table 5. Fractionation of the products yielded:

Fraction I, b.p. 60-63° (37 mm); $n_D^{18.5}$ 1.4465; 42.0 g

Fraction II, b.p. 58-139° (24 mm); $n_D^{18.5}$ 1.4480; 1.1 g

Fraction III, b.p. 139-143° (24 mm); $n_D^{18.5}$ 1.4555; 19.6 g

After a second fractionation, Fraction I came over completely at 64-64.5° (40 mm), and was found to be 2-propoxyethanethiol $C_3H_7OCH_2CH_2SH$, obtained in 60.8% yield (for properties and analysis see Table 1). The mercurichloride $C_3H_7OCH_2CH_2SHgCl$ (fine white crystals) after recrystallization from boiling ethanol melted at 137-137.5° (see Table 2).

Fraction III consisted of a mixture of the sulfides $(C_3H_7OCH_2CH_2)_2S$ and $C_3H_7OCH_2CH_2SCH(OC_3H_7)CH_3$, for it gave a white precipitate with an ethanolic solution of mercuric chloride, and at the same time turned Methyl Orange red [6]. The content of 1,2'-isomer was found by titration to be 14.1%. After a second fractionation from a Favorsky flask, this mixture had: b.p. 103-106° (4 mm); n_D^{20} 1.4548; d_4^{20} 0.9326; found MR 60.01, calculated MR 59.73.

Found %: C 58.07; 58.37; H 10.87; 10.91; S 15.36; 15.47
 Calculated %: C 58.20; H 10.75; S 15.54

* No depression in admixture with our previously prepared sample [6].

TABLE 3

No.	Formula	B.p. in °C (pressure in mm Hg)	n_D^{20}	d_4^{20}	MR		Analysis					M.p. of com- plex salt with HgCl ₂ (°C)
					found	calculated	found			calculated		
							C	H	S	C	H	
1	(C ₂ H ₅ OCH ₂ CH ₂) ₂ S	83.8-84.4 (3.5)	1.4560	0.9550	50.70	50.40	-	-	-	-	-	93-93.5
2	(n C ₃ H ₇ OCH ₂ CH ₂) ₂ S	105.8 (4)	1.4553	0.9394	59.69	59.75	-	-	-	-	15.54	69-70
3	(iso-C ₃ H ₇ OCH ₂ CH ₂) ₂ S	99-99.5 (6.0)	1.4493	0.9258	59.85	59.75	{58.45 58.38	{10.79 10.82	{15.50 15.22	10.75	15.54	91-91.5
4	(n C ₄ H ₉ OCH ₂ CH ₂) ₂ S	130-131 (4.9)	1.4560	0.9224	69.00	68.88	-	-	-	-	-	Liquid
5	(iso-C ₄ H ₉ OCH ₂ CH ₂) ₂ S	125-126 (5)	1.4506	0.9130	69.13	68.88	-	-	-	-	-	47
6	(iso-C ₅ H ₁₁ OCH ₂ CH ₂) ₂ S	144-145 (4)	1.4550	0.9089	78.49	78.1	-	-	-	-	-	Liquid
7	(n C ₆ H ₁₃ OCH ₂ CH ₂) ₂ S	195-198 (3-3.5)	1.4610	0.8952	106.25	105.82	{69.53 69.37	{12.32 12.56	{9.45 9.24	12.22	9.25	Liquid
8	(C ₆ H ₁₁ OCH ₂ CH ₂) ₂ S (cyclohexyl)	182-184 (5)	1.4982	1.0112	83.06	82.94	{66.96 66.78	{10.80 10.51	{11.21 11.19	10.55	11.20	118

We made no attempt to fractionate this mixture, although we have already shown [6] that the separation of such sulfides by distillation is quite feasible, if a sufficiently efficient column is used.

The pure bis(2-propoxyethyl) sulfide was obtained by precipitating the whole of the 1,2'-isomer by means of mercuric chloride (see [6]). This was carried out by addition of 13 ml of a 20% solution of HgCl₂ in ethanol (slight excess over the amount of 1,2'-isomer present) to 12.2 g of this mixture of sulfides. The precipitate of the mercurichloride was filtered off after three days, and, after two crystallizations from boiling ethanol, it melted at 137-137.5° and gave no depression in admixture with the derivative obtained from the thiol. The filtrate was diluted with two parts of diethyl ether, and this solution was washed, first with water and then with caustic soda solution; the precipitate of HgO was filtered off, and the ether layer was again washed with water and then dried over calcined sodium sulfate.

Removal of ether yielded pure bis(2-propoxyethyl) sulfide having the constants given in Table 3; its complex salt with mercuric chloride melted at 69-70°. For bis(2-propoxyethyl) sulfide prepared by the action of zinc dust on bis(2-chloroethyl) sulfide in propyl alcohol, the literature [11] gives b.p. 243-247° (761 mm); n_D^{20} 1.4573; d_4^{20} 0.9439 and m.p. of the salt (C₃H₇OCH₂CH₂)₂S·HgCl₂ -71°.

The main products of the reaction between H₂S and propyl vinyl ether were 2-propoxyethanethiol and bis(2-propoxyethyl) sulfide.

III. Addition of Hydrogen Sulfide to Isopropyl Vinyl Ether

The results given in Table 6 show that under the experimental conditions used isopropyl vinyl ether again gives mainly products of addition in the direction contrary to Markovnikov's rule. The amount of the 1,2'-isomer iC₃H₇OCH₂CH₂SCH(iC₃H₇O)CH₃ in the sulfide mixture was, however, somewhat higher than for the n-propyl vinyl ether.

IV. Addition of Hydrogen Sulfide to Isobutyl Vinyl Ether

The experimental results are given in Table 7.

In Experiments Nos. 1, 3, 4, and 5 the thiol fraction

contained some 1-isobutoxyethanethiol $\text{CH}_3\text{CH} \begin{matrix} \nearrow \text{OC}_4\text{H}_9 \\ \searrow \text{SH} \end{matrix}$

for after the first fractionation it gave a yellowish precipitate with mercuric chloride [6, 12]. The same applies to the sulfide fractions, evidently contained mixtures of 2,2'-, 1,2'-, and 1,1'-isomers, so that it was not possible to determine their true compositions by titration [6]. Owing to the content of 1-alkoxy thiol in the thiol mixture, the actual percentage of the H₂S molecules adding in the "α" position was somewhat higher than that given in the last column, which is based on titration results. The yield of "normal" addition products was considerably higher for isobutyl vinyl ether than for other ethers, particularly in

TABLE 4

Expt. No.	Amount taken		Duration of expt. (days)	Ether recovered (g)	Yield of reaction products (%)			Amount of 1,2'-sulfide in sulfide fr. (%)	α -Addition of H ₂ S (%)
	of ether (g)	of H ₂ S (moles per mole of ether)			thiol	sulfide	total		
1	20	1.4	60	1.1	57.4	23.9	81.3	~1	<1
2	25	0.4	10	14.0	38.3	35.4	73.7	1.3	~0.5
3	15	1.4	10	—	58.9	27.5	86.4	7.7	~2

experiments in which the H₂S concentration was high (Expt. No. 1 and 3), and the reaction rate was considerably lower (see Expt. No. 6). The ether used in Expt. No. 5 was preserved for six months over sodium and then distilled once before the experiment; it gave a distinct peroxide reaction. In this experiment addition was very much retarded, and the percent " α -addition" was very high.

V. Addition of Hydrogen Sulfide to Isopentyl Vinyl Ether

Isopentyl vinyl ether reacts very slowly with hydrogen sulfide (Expt. No. 1 and 5, Table 8). In all experiments the thiol fractions gave slightly yellowish precipitates with mercuric chloride, indicating the presence of 1-isopentyl-

oxyethanethiol $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OC}_5\text{H}_{11} \\ \text{SH} \end{smallmatrix}$ [6, 12], as in the case of isobutyl vinyl ether, so that the actual proportion of

H₂S molecules adding in the α -position was somewhat higher than that calculated from results of the titration of the sulfide fraction. A particularly high content of " α -addition" products was given by the ether that had been kept for a long time over sodium (see Expt. No. 2). In this experiment the sulfide fraction contained not less than 32% of the 1,1'-isomer, which as shown previously [12], yields two molecules of HCl when treated with mercuric chloride. The thiol fraction, b.p. 38-48° at 4 mm, gave an egg-yellow precipitate with mercuric chloride, i.e.,

consisted mainly of the thiol $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OC}_5\text{H}_{11} \\ \text{SH} \end{smallmatrix}$. Ascaridol (Expt. No. 7) did not appreciably accelerate the

reaction between hydrogen sulfide and isopentyl vinyl ether at room temperature.

TABLE 5

Expt. No.	Amount taken		Experimental conditions			Ether recovered (g)	Yield of reaction products (%)			Amt. of 1,2'-sulfide in sulfide fr. (%)	α -Addition of H ₂ S (%)
	of ether (g)	of H ₂ S (moles per mole of ether)	total duration (days)	temp. at which heated (°C)	duration of heating (hr.)		thiol	sulfide	total		
1	49.5	1.2	65	—	—	—	60.8	33.1	93.9	14.1	5
2	15.0	2.9	97	—	—	—	80.0	16.1	96.1	19.2	3
3	15.0	2.6	5	70	18	0.2	70.5	18.1	88.6	47.4	14
4	15.0	0.5	5	70	18	3.1	29.2	56.1	85.3	11.7	6

VI. Addition of Hydrogen Sulfide to Octyl Vinyl Ether

The experiments in Table 9 show that, in presence of traces of oxygen, octyl vinyl ether unites slowly with hydrogen sulfide, but almost entirely in the direction contrary to Markovnikov's rule. When attempts were made to accelerate the reaction by introduction of an HCl-dioxane catalyst (Expt. No. 2 and 3), an appreciable yield of "normal" addition products was obtained.

VII. Addition of Hydrogen Sulfide to Cyclohexyl Vinyl Ether

As will be seen from Table 10, cyclohexyl vinyl ether unites with hydrogen sulfide still more slowly than isopentyl vinyl ether does, and it gives a still higher yield of addition products formed in accordance with Markovnikov's rule.

In Expt. Nos. 4-6 catalyst (27% HCl in dioxane) was added. In Expt. Nos. 3, 4, and 5, apart from the thiol and sulfide indicated in the tables, decomposition products were obtained: cyclohexanol, b.p. 160-162°, and a high-boiling residue, which decomposed when distilled and corresponded closely in analysis to the mercaptal $\text{CH}_3\text{CH}(\text{SCH}_2\text{CH}_2\text{OC}_6\text{H}_{11})_2$.

TABLE 6

Expt. No.	Amount taken		Experimental conditions			Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfide in sulfide fr. (%)	α -Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated ($^{\circ}C$)	duration of heating (hr.)		thiol	sulfide	total		
1	28.2	1.1	68	-	-	-	58.5	35.0	93.5	28.5	~10
2	10.0	0.5	12	70	26	3.8	-	89.2	89.2	10.6	~9
3	20.5	2.0	12	70	26	-	70.2	19.1	89.3	22.6	~4

TABLE 7

Expt. No.	Amount taken		Experimental conditions			Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfide in sulfide fr. (%)	α -Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated ($^{\circ}C$)	duration of heating (hr.)		thiol	sulfide	total		
1	15	2.3	8	70	27	-	54.2	25.0	79.2	70.1	>17
2	15	0.5	9	70	27	3.5	31.3	66.2	97.5	19.5	~13
3	20	1.0	12	70	58	-	34.3	51.7	86.0	45.5	>23
4	15	1.4	63	Room	-	-	36.7	51.1	87.8	29.5	>15
5	62	0.9	60	"	-	40.9	48.3	14.9	63.2	62.7	>9
6	15	1.3	14	"	-	12.0	27.5	28.5	65.0	Not determined	

TABLE 8

Expt. No.	Amount taken		Experimental conditions		Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfoxide in sulfide fr. (%)	α -Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated ($^{\circ}C$)		thiol	sulfide	total		
1	20.0	0.7	75	—	18.9	77.0	—	77.0	—	—
2	40.0	2.4	64	—	—	44.4	43.8	88.2	131.8	~100
3	14.7	1.3	6	70	8.1	58.4	21.1	79.5	64.2	> 13
4	20.0	1.3	30	70	116	61.3	28.6	89.9	37.2	> 11
5	18.4	0.6	45	70	13.5	—	78.0	78.0	10.6	~ 8
7	20.0	0.7	7	—	18.5	—	—	—	—	—

TABLE 9

Expt. No.	Amount taken		Experimental conditions		Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfoxide in sulfide fr. (%)	α -Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated ($^{\circ}C$)		thiol	sulfide	total		
1	40.0	1.95	90	—	3.0	69.0	21.4	90.4	—	—
2	20.0	1.05	10	$\begin{cases} 60 \\ 40 \end{cases}$	2.1	35.8	60.4	96.2	50.0	30
3	15.0	0.5	18	$\begin{cases} 60 \\ 40 \end{cases}$	1.8	5.6	77.0	82.6	17.0	13

TABLE 10

Expt. No.	Amount taken		Experimental conditions		Ether recovered (g)	Yields of reaction products (%)			Amount of 1,2'-sulfoxide in sulfide fr. (%)	α -Addition of H_2S (%)
	of ether (g)	of H_2S (moles per mole of ether)	total duration (days)	temp. at which heated ($^{\circ}C$)		thiol	sulfide	total		
1	30.0	1.2	150	—	10.0	65.8	20.3	86.1	88.6	18
2	30.0	0.6	150	—	18.8	57.6	24.3	81.9	66.4	15
3	20.0	1.0	35	60	0.8	16.5	48.0	64.5	91.7	44
4	29.5	1.0	27	60	—	8.3	52.3	60.6	90.4	~50
5	24.0	0.9	12	60	—	19.7	37.4	57.1	104.4	~40
6	20.0	0.4	13	60	—	—	71.8	71.8	21.6	~15

SUMMARY

1. Reaction of hydrogen sulfide with ethyl, propyl, isopropyl, isobutyl, octyl, isopentyl, and cyclohexyl vinyl ethers yielded 2-alkoxyethanethiols and mixtures of sulfides containing various proportions of the isomeric dialkoxo diethyl sulfides. Addition products formed in violation of Markovnikov's rule predominated in the reaction mixtures, particularly in the case of ethers having normal alkyl radicals. Ethers having branched (isopentyl) and cyclic (cyclohexyl) radicals gave particularly high yields of "normal" addition products.

2. A general method is given for the synthesis of 2-alkoxyethanethiols $\text{ROCH}_2\text{CH}_2\text{SH}$ in 55-80% yield from the corresponding vinyl ethers.

3. It is suggested that the ratio of Markovnikov and anti-Markovnikov addition products is related to the tendency of the vinyl ether to react by an ionic mechanism.

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* See Consultants Bureau Translation, page 235.

** See Consultants Bureau Translation, page 453.

*** See Consultants Bureau Translation, page 325.

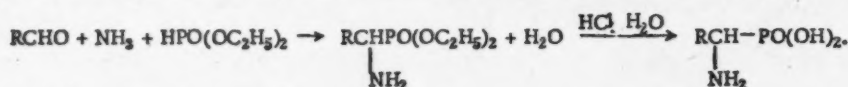
**** See Consultants Bureau Translation, page 459.

NEW METHOD FOR THE SYNTHESIS OF AMINO PHOSPHONIC ACIDS

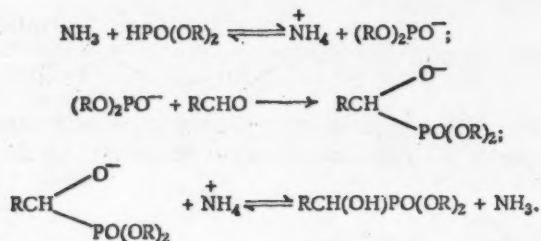
COMMUNICATION 2. REACTION OF KETONES WITH DIALKYL PHOSPHITES AND AMMONIA

T. Ya. Medved and M. I. Kabachnik

We have recently described a new method for the synthesis of aminoalkylphosphonic acids by reaction of aldehydes with dialkyl phosphites and ammonia [1]. We in fact found that, when dialkyl phosphites are heated with an alcoholic solution of ammonia and aldehydes, esters of the corresponding amino phosphonic acids are formed; hydrolysis of the esters then results in the formation of free amino phosphonic acids:



Owing to its simplicity, this synthesis has made possible the preparation of a number of substances hitherto inaccessible. In the preceding communication, we described the preparation of a number of aliphatic-aromatic amino phosphonic acids from aromatic aldehydes and diethyl or dibutyl phosphite, and also a number of experiments carried out with the object of elucidating the mechanism of the reaction. We showed that in presence of ammonia aldehydes react in the cold with dialkyl phosphites with formation of esters of hydroxyalkylphosphonic acids. Since this reaction was catalyzed also by hydroxyl ions [2], we considered that in our reaction, the ammonia acted as a basic catalyst:

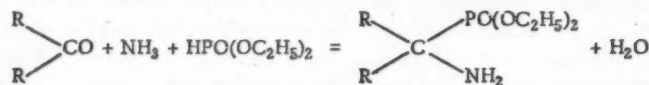


When the reaction mixture was heated, the second stage of the reaction — replacement of the hydroxyl of the hydroxyalkylphosphonic ester by amino— took place:



Great interest was presented by the possibility of extending the new reaction to ketones.

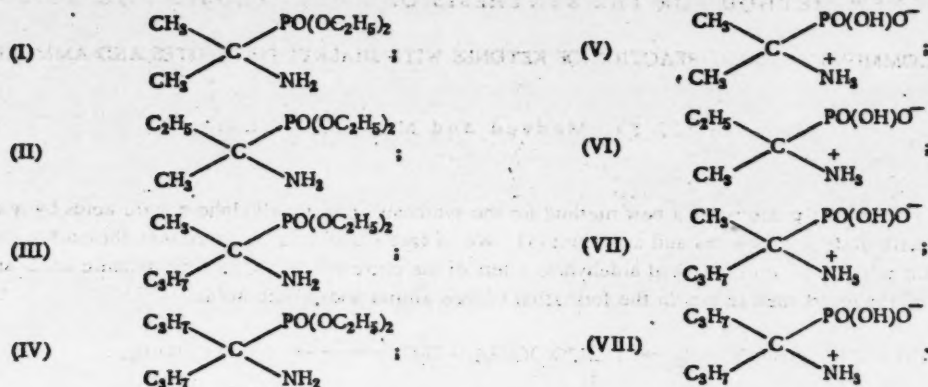
In the present investigation, we have shown that our reaction occurs also in the ketone series. Dialkyl phosphites react with ammonia and ketones much more readily than they do with ammonia and aldehydes. A shorter period of heating is required for the completion of the reaction, and in a number of cases heating in sealed tubes may be replaced by passage of ammonia into the heated reaction mixture. By the condensation of ketones with dialkyl phosphites and ammonia, amino phosphonic esters having a secondary carbon



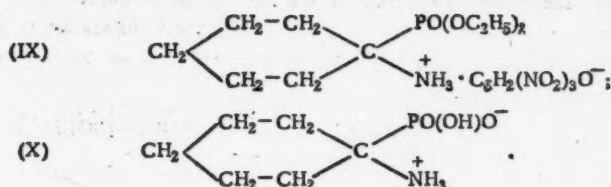
and the corresponding acids — substances that have previously been difficultly accessible— may now be prepared.

The reaction is applicable not only to aliphatic and alicyclic ketones, but also to aliphatic-aromatic and purely aromatic ketones. The aliphatic ketones react the most readily. Acetone, 2-butanone, 2-pentanone, and 4-heptanone will react with an equivalent amount of diethyl phosphite and 10% alcoholic ammonia when heated in sealed tubes in a boiling water bath for three hours. Practically the same results can be obtained by passing dry gaseous ammonia for 5-6 hours through a refluxed mixture of the ketone and diethyl phosphite. The products are the esters of 1-amino-1-methylethylphosphonic acid (I), 1-amino-1-methylpropylphosphonic acid (II), 1-amino-1-methylbutylphosphonic acid (III), and 1-amino-1-propylbutylphosphonic acid (IV). These products are obtained in yields of about 40%. They can be isolated from the reaction

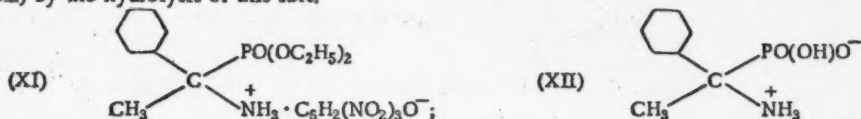
mixture either in the form of salts (picrates or hydrochlorides), or in the free state by vacuum distillation. When they are heated with diluted (1:1) hydrochloric acid in sealed tubes at 110-120°, the ester groups are hydrolyzed and the corresponding free amino phosphonic acids (V, VI, VII, and VIII) are formed:



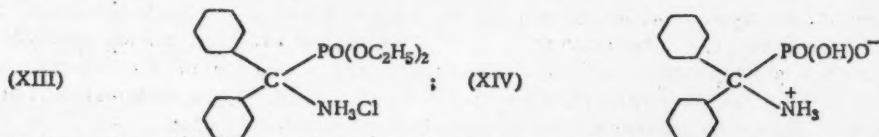
Allicyclic and aliphatic-aromatic ketones react with greater difficulty. Thus, cyclohexanone under the same conditions, but heated in the sealed tube for seven hours, forms the corresponding ester of 1-aminocyclohexylphosphonic acid, which was isolated as the picrate (IX); from the latter the free amino phosphonic acid (X) was obtained:



Reaction with acetophenone also requires longer heating; it yields the ester of 1-amino-1-phenylethylphosphonic acid in 20-25% yield. We again isolated this as the picrate (XI) and obtained the free amino phosphonic acid (XII) by the hydrolysis of this salt:

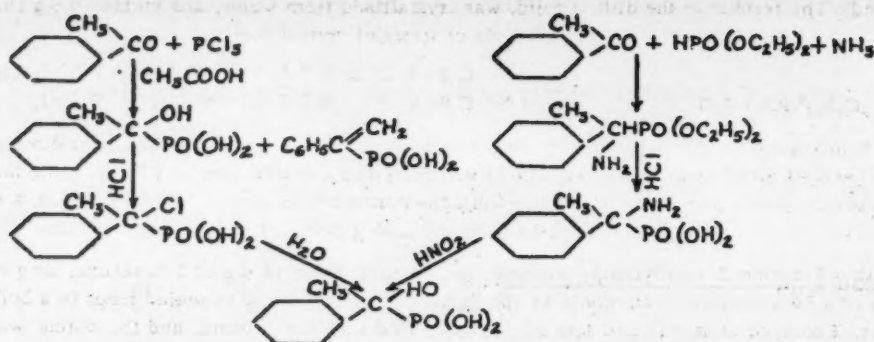


Benzophenone was the least ready to react. Treatment of the reaction mixture gave the hydrochloride of aminodiphenylmethylphosphonic ester (XIII) in a yield of only 13%. The free aminodiphenylmethylphosphonic acid (XIV) was prepared by heating the hydrochloride with hydrochloric acid:



All of the free amino phosphonic acids that we obtained are actually internal salts; they are colorless high-melting crystalline substances, and crystallize from water with one or two molecules of water of crystallization. The amino group of an amino phosphonic acid can readily be converted into a hydroxyl group by the action of nitrous acid. We generally determined the amino nitrogen in the synthesized compounds by the Van Slyke method.

We converted our 1-amino-1-phenylethylphosphonic acid (XII) into 1-hydroxy-1-phenylethylphosphonic acid by the action of nitrous acid in aqueous solution. The latter compound has been prepared previously by Conant [3] from benzaldehyde and phosphorus trichloride; the mixture of hydroxy acid and unsaturated acid at first formed was converted by Conant into the chloro acid by the action of hydrogen chloride, and this was isolated in the pure state and then carefully hydrolyzed to the hydroxy acid. We repeated this synthesis and obtained 1-hydroxy-1-phenylethylphosphonic acid. Comparison of the two specimens of hydroxy acid obtained by different methods showed them to be identical:



Both specimens melted at 149° , and a mixture test showed no depression. The analyses also gave confirmation of the identity of the two substances. The structure of the amino acid and the general scheme of our reaction are confirmed by this preparation of a hydroxy acid of known structure from our amino acid.

EXPERIMENTAL

Diethyl 1-amino-1-methylethylphosphonate. 1) A mixture of 15 g of acetone, 35 g of diethyl phosphite, and 75 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. Excess of alcohol and ammonia was distilled from the reaction mixture, and the residue was vacuum-distilled. After two fractionations, two fractions were obtained:

Fraction I, b.p. $45-46^\circ$ (3 mm); n_D^{20} 1.4062; d_4^{20} 1.0676; 3.1 g

Fraction II, b.p. $65-66^\circ$ (3 mm); n_D^{20} 1.4327; d_4^{20} 1.0437; 24.3 g

The first fraction was found to be impure unchanged diethyl phosphite. The second fraction, a light-yellow liquid, was diethyl 1-amino-1-methylethylphosphonate, obtained in 47.5% yield. Found MR 48.5. Calculated MR 48.8.

	Found %:	C 43.1; 43.0;	H 9.7; 9.5;	P 15.6; 15.9;	N 7.5; 7.6
$\text{C}_7\text{H}_{18}\text{NPO}_3$	Calculated %:	C 43.1;	H 9.2;	P 15.9;	N 7.2

2) A mixture of 12 g of acetone and 28 g of diethyl phosphite was placed in a three-necked flask fitted with reflux condenser, thermometer, and tube for passage of gas. Dry ammonia was passed through the mixture, and the temperature rose to 48° . When the temperature had fallen again, the mixture was heated for three hours in a water bath at 50° , and then for two hours in a boiling water bath. The reaction mixture was vacuum-distilled. After two distillations, two fractions were obtained:

Fraction I, b.p. $62-67^\circ$ (4 mm); n_D^{20} 1.4063; 2.8 g

Fraction II, b.p. $66-67^\circ$ (3 mm); n_D^{20} 1.4333; d_4^{20} 1.0432; 17.0 g

Yield 42.5%. Found MR 48.6. Calculated MR 48.8.

Picrate of diethyl 1-amino-1-methylethylphosphonate. A mixture of 3 g of acetone, 7 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. The reaction mixture was then evaporated down in a porcelain dish on a boiling water bath until a constant residue was obtained. The syrupy yellow residue was dissolved in 20 ml of ethanol, and an ethereal solution of picric acid was added. The picrate was recrystallized from absolute ethanol; 8.7 g (40%) was obtained, m.p. 175° .

	Found %:	C 36.9; 37.1;	H 4.7; 4.9;	N 13.5; 13.2;	P 7.1; 7.2
$\text{C}_{13}\text{H}_{21}\text{H}_4\text{PO}_{10}$	Calculated %:	C 36.8;	H 4.9;	N 13.2;	P 7.3

1-Amino-1-methylethylphosphonic acid. 1) A mixture of 2 g of the picrate of diethyl 1-amino-1-methylethylphosphonate, m.p. 175° , and 40 ml of hydrochloric acid (1:1) was heated in sealed tubes at $120-125^\circ$ for three hours. Then, in order to remove picric acid, the contents of the tubes were extracted with ether until the aqueous layer was decolorized. The aqueous layer was evaporated on a boiling water bath until the odor of HCl

disappeared. The residue in the dish, a solid, was crystallized from water, and yielded 0.6 g (91%) of a colorless crystalline substance. It contained one molecule of water of crystallization.

	Found %	C 23.4; 23.2;	H 7.5; 7.5;	N 9.1; 8.9;	P 19.7; 19.8;	H ₂ O 11.7
$C_3H_{10}NPO_3 \cdot H_2O$	Calculated %	C 22.9	H 7.6;	N 8.9;	P 19.7;	H ₂ O 11.5

2) A mixture of 3 g of diethyl 1-amino-1-methylethylphosphonate (b.p. 65-66° at 3 mm; n_D^{20} 1.4327; d_4^{20} 1.0437) and 45 ml of hydrochloric acid (1:1) was heated in a sealed tube at 120° for three hours. The reaction mixture was evaporated to constant weight and disappearance of the odor of HCl in a dish on a water bath. The dry residue was recrystallized from water, and yielded 1.95 g (90%) of substance of m.p. 258°.

Diethyl 1-amino-1-methylpropylphosphonate. A mixture of 14.4 g of 2-butanone, 28 g of diethyl phosphite, and 60 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. Excess of ammonia and alcohol were distilled from the mixture, and the residue was vacuum-distilled. After two distillations the following fractions were obtained:

Fraction I, b.p. 42-45° (3 mm); n_D^{20} 1.4069; 4.8 g

Fraction II, b.p. 87-88° (5 mm); n_D^{20} 1.4397; d_4^{20} 1.0381; 15.1 g

The first fraction was found to be impure unchanged diethyl phosphite. The second fraction, a light-yellow liquid, was diethyl 1-amino-1-methylpropylphosphonate, obtained in 36% yield. Found MR 53.1. Calculated MR 53.4

	Found %	N 6.2; 6.2;	P 14.7; 14.8;	C 46.2; 46.2;	H 9.7; 9.7
$C_4H_{12}NPO_3$	Calculated %	N 6.7;	P 14.8;	C 45.9;	H 9.6

Picrate of diethyl 1-amino-1-methylpropylphosphonate. A mixture of 3.6 g of 2-butanone, 7 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for three hours. The reaction mixture was then evaporated in a porcelain dish on a boiling water bath to constant weight. The yellow syrupy residue was dissolved in 20 ml of ethanol, and an ethereal solution of picric acid was added until precipitation of the picrate was complete. The picrate was filtered off and recrystallized from absolute ethanol, yielding 6.2 g (28%) of a yellow crystalline substance, m.p. 166°.

	Found %	N 3.3; 3.2;	P 7.1; 7.3
$C_{14}H_{23}NP_2O_{10}$	Calculated %	N 3.2;	P 7.1

1-Amino-1-methylpropylphosphonic acid. 1) A mixture of 3 g of diethyl 1-amino-1-methylpropylphosphonate and 40 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120° for three hours. The reaction mixture was evaporated to constant weight and disappearance of the odor of HCl on a boiling water bath. The dry residue was recrystallized from a mixture of water and alcohol, and yielded 1.4 g (57%) of a colorless crystalline substance, which decomposed at 262°. It crystallized with one molecule of water.

	Found %	P 18.1; 18.2;	N 8.3; 8.3;	H ₂ O 10.7
$C_4H_{12}NPO_3 \cdot H_2O$	Calculated %	P 18.1;	N 8.2	H ₂ O 10.5

2) A mixture of 2 g of the picrate of diethyl 1-amino-1-methylpropylphosphonate (m.p. 166°) and 40 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120-130° for three hours. The contents of the tubes were extracted with water until the water layer was decolorized. The water layer was evaporated on a boiling water bath until the odor of HCl disappeared. The solid residue in the dish was recrystallized from water, and yielded 0.45 g (65%) of a colorless crystalline substance, m.p. 262°.

	Found %	P 18.2; 18.2;	N 7.9; 7.9;	H ₂ O 10.3
$C_4H_{12}NPO_3 \cdot H_2O$	Calculated %	P 18.1;	N 8.2;	H ₂ O 10.5

Diethyl 1-amino-1-methylbutylphosphonate. A mixture of 4.3 g of 2-pentanone, 7 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated for three hours in a boiling water bath. The reaction mixture was vacuum-fractionated. Two distillations yielded the following fractions:

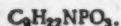
Fraction I, b.p. 36-40° (2 mm); n_D^{20} 1.4065; 6.1 g

Fraction II, b.p. 82-83° (2 mm); n_D^{20} 1.4400; d_4^{20} 1.0320; 16.4 g

Yield 32.2%.

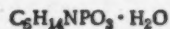
The first fraction was impure diethyl phosphite. The second fraction was a slightly yellowish mobile liquid having a feeble odor. Found MR 57.0. Calculated MR 58.0.

Found %: C 48.3; 48.2; H 10.2; 10.1; P 14.0; 13.9
 Calculated %: C 48.4; H 9.9; P 13.9



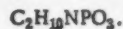
1-Amino-1-methylbutylphosphonic acid. A mixture of 3 g of diethyl 1-amino-1-methylbutylphosphonate and 60 ml of hydrochloric acid (1:1) was heated in sealed tubes at 120-130° for three hours. The reaction mixture was evaporated down to constant weight and until the odor of HCl disappeared. The dry residue was recrystallized from a mixture of water and alcohol, and yielded 1.4 g (56%) of a colorless crystalline substance, which crystallize with one molecule of water and decomposed at 262-263°.

Found %: C 32.4; 32.4; H 9.1; 9.2; P 16.8; 16.9; N 7.7; 7.6; H₂O 9.95
 Calculated %: C 32.4; H 8.7; P 16.8; N 7.6; H₂O 9.73



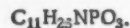
Diethyl 1-amino-1-propylbutylphosphonate. Dry ammonia was passed for one hour at room temperature into a mixture of 11.4 g of 4-heptanone (b.p. 142-144°; n_D^{20} 1.4045) and 14 g of diethyl phosphite; no rise of temperature was observed. The reaction mixture was then heated in a water bath at 50° for three hours, and then for two hours in a boiling water bath. On cooling, the reaction mixture partially crystallized out. The crystals were filtered off and washed with dry ether (3.8 g of a colorless crystalline substance, m.p. 95°). The substance was an ammonium salt, for treatment with alkali resulted in the immediate evolution of ammonia. The analysis corresponded to the ammonium salt of monoethyl phosphite:

Found %: C 19.3; 19.3; H 7.8; 7.9; P 24.8; 24.7
 Calculated %: C 18.9; H 7.8; P 24.4



The filtrate from the separation of the crystals was vacuum-fractionated, and after two distillations 8.2 g (33%) of a fraction of b.p. 106-108° at 3 mm was isolated: n_D^{20} 1.4447; d_4^{20} 1.0034; Found MR 66.54. Calculated MR 67.2.

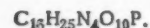
Found %: C 52.5; 52.8; H 10.4; 10.5; P 12.4; 12.3; N 6.0; 6.1
 Calculated %: C 52.6; H 10.4; P 12.4; N 5.6



1-Amino-1-propylbutylphosphonic acid. A mixture of 4 g of the ethyl ester obtained in the preceding experiment and 60 ml of hydrochloric acid (1:1) was heated in a sealed tube at 120° for three hours. The reaction mixture was evaporated to constant weight and disappearance of the odor of HCl on a boiling water bath. The syrupy residue was dried for several days in a desiccator over phosphoric anhydride, and it then crystallized out. It was recrystallized from a mixture of absolute ethanol and ethyl acetate. The product was 2.1 g of colorless crystals, m.p. 192°.

Picrate of diethyl 1-aminocyclohexylphosphonate. A mixture of 5.7 g of cyclohexanone, 8 g of diethyl phosphite, and 15 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. The reaction mixture was then evaporated in a dish to constant weight in a boiling water bath. The syrupy residue was dissolved in 20 ml of ethanol, and an ethereal solution of picric acid was added until precipitation was complete. Recrystallization of the precipitate from absolute ethanol yielded 5.6 g (19%) of substance, m.p. 172°.

Found %: C 41.4; 41.5; H 5.7; 5.4; N 12.2; 12.3; P 6.8; 6.9
 Calculated %: C 41.4; H 5.4; N 12.1; P 6.7



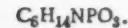
1-Aminocyclohexylphosphonic acid. A mixture of 1 g of the picrate of diethyl 1-aminocyclohexylphosphonate and 20 ml of hydrochloric acid (1:1) was heated in a sealed tube at 120-130° for three hours. The contents of the tubes were then extracted with ether until the aqueous layer was decolorized. The aqueous layer was evaporated on a water bath until the odor of HCl disappeared. The solid remaining in the dish was recrystallized from water, and yielded 0.35 g (91%) of colorless crystals, m.p. 238°. The substance crystallized with one molecule of water.

Found %: C 36.8; 36.5; H 7.8; 7.9; N 6.9; 7.0; P 15.6; 15.4; H₂O 9.16
 Calculated %: C 36.5; H 8.1; N 7.1; P 15.7; H₂O 9.15



After being dried at 150°, the substance was again analyzed:

Found %: C 40.1; 40.2; H 7.7; 7.6
 Calculated %: C 40.2; H 7.8



Picrate of diethyl 1-amino-1-phenylethylphosphonate. A mixture of 12 g of acetophenone, 14 g of diethyl phosphite, and 25 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. Excess of alcohol and ammonia was removed under reduced pressure. The residue was dissolved in dry ether (20-30 ml), and an ethereal solution of picric acid was added. The precipitated picrate was recrystallized from absolute ethanol; 16.2 g (33%), m.p. 174-175°, was obtained.

Found %: N 11.4; 11.2; P 6.1; 6.4
 $C_{13}H_{23}N_4PO_8$ Calculated %: N 11.5; P 6.4

1-Amino-1-phenylethylphosphonic acid. A mixture of 7 g of the picrate of diethyl 1-amino-1-phenylethylphosphonate and 140 ml of hydrochloric acid (1:1) was heated in sealed tubes for three hours at 130-135°. The contents of the tubes were extracted with ether until the aqueous layer was decolorized. The aqueous layer was evaporated on a boiling water bath until the odor of HCl completely disappeared. The solid residue was recrystallized from water (it was dissolved in about 700 ml of water after long boiling, and the solution was then evaporated to one-tenth of its original volume). The product was 2.65 g (81%) of a slightly yellowish crystalline substance, m.p. 235°; it crystallized with one molecule of water.

Found %: P 14.6; 14.4; N 6.4; 6.5; H_2O 8.3
 $C_8H_{12}NPO_3 \cdot H_2O$ Calculated %: P 14.2; N 6.4; H_2O 8.2

Reaction of 1-amino-1-phenylethylphosphonic acid with nitrous acid. Nitrogen oxides were passed through an ice-cooled solution of 1 g of 1-amino-1-phenylethylphosphonic acid in 500 ml of water. Several minutes after passage of the gas, bubbles of gas began to separate throughout the whole liquid. Nitrogen oxides were passed for four hours, until formation of gas bubbles stopped completely. Toward the end of the reaction the solution was heated to 50° for 30 minutes. The solution was then evaporated under reduced pressure, the bath temperature not exceeding 40-50°. The syrupy residue was dried in a vacuum desiccator over calcium chloride and caustic potash. It then crystallized out, and was recrystallized from a mixture of dry ether and chloroform. After a few recrystallizations it melted at 149°. A mixture melting point with 1-hydroxy-1-phenylethylphosphonic acid prepared by Conant's method [3] (m.p. 150°) showed no depression.

Found %: C 47.8; 47.7; H 5.8; 5.5; P 15.7; 15.3
 $C_8H_{11}PO_4$ Calculated %: C 47.5; H 5.5; P 15.3

Hydrochloride of diethyl aminodiphenylmethylphosphonate. A mixture of 13.5 g of benzophenone, 10 g of diethyl phosphite, and 23 ml of a 10% solution of ammonia in absolute ethanol was heated in sealed tubes in a boiling water bath for seven hours. The contents of the tubes were then evaporated to constant weight on a boiling water bath. The residue consisted of two liquid layers, which readily solidified on standing; they were separated and treated separately. The lower layer was found to be a mixture of ammonium salts of phosphorus acids, and it was not investigated further. The upper layer was dissolved in dry ether, and into the solution, cooled with ice water, hydrogen chloride was passed. The ether and excess of hydrogen chloride was removed under reduced pressure at room temperature, the ether that distilled off being periodically replaced by fresh ether to bring the volume to its initial value. After removal of hydrogen chloride, the ether solution yielded colorless crystals of the hydrochloride, and the unchanged benzophenone remained in the ether. The crystals were filtered off, washed with ether, and recrystallized from a mixture of ether and alcohol, yielding 3.5 g (13%) of a colorless crystalline substance, m.p. 144°.

Found %: N 4.4; 4.5; P 8.3; 8.0
 $C_{17}H_{23}O_3NPCl$ Calculated %: N 3.9; P 8.7

Aminodiphenylmethylphosphonic acid. A mixture of 1.8 g of the hydrochloride of diethyl aminodiphenylmethylphosphonate and 36 ml of hydrochloric acid (1:1) was heated in sealed tubes at 110-120° for three hours. The contents of the tubes were then evaporated on a boiling water bath until the odor of HCl completely disappeared. The residue was recrystallized from aqueous alcohol, and yielded 1.2 g (90%) of a colorless crystalline substance, m.p. 232°; it crystallized with two molecules of water.

Found %: N 4.9; 4.9; P 10.5; 10.3; H_2O 11.8
 $C_{13}H_{14}PNO_3 \cdot 2H_2O$ Calculated %: N 4.7; P 10.4; H_2O 12.0

SUMMARY

1. It has been shown that our condensation reaction between dialkyl phosphites, aldehydes, and ammonia can be extended also to ketones. The reaction can be applied not only to aliphatic and alicyclic ketones, but also to aliphatic-aromatic and purely aromatic ketones. The reaction of dialkyl phosphites with ammonia and

ketones results in the formation of esters of α -amino phosphonic acids having a branched radical.

2. A simple method has been developed for the preparation of amino phosphonic acids by the action of ketones on dialkyl phosphites and ammonia, and hydrolysis of the esters so formed.

3. The following substances have been synthesized and characterized: 1-amino-1-methylethylphosphonic acid, 1-amino-1-methylpropylphosphonic acid, 1-amino-1-methylbutylphosphonic acid, 1-amino-1-propylbutylphosphonic acid; 1-aminocyclohexylphosphonic acid, 1-amino-1-phenylethylphosphonic acid, and aminodiphenylmethylphosphonic acid, and also their esters, and the hydrochlorides and picrates of these esters.

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SYNTHESIS AND REACTIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 4. COPOLYMERIZATION OF 2-VINYLOXYETHYLAMINE WITH METHYL METHACRYLATE

M. F. Shostakovskiy, I. A. Chekulaeva, and A. M. Khomutov

We have pointed out in previous communications [1, 2, 3] that 2-vinyloxyethylamine $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{NH}_2$ differs from alkyl vinyl ethers in chemical properties: it has a considerably lower tendency to undergo reactions that proceed by an ionic mechanism. This behavior of 2-vinyloxyethylamine is to be explained by the association in its molecule of the double bond with two centers capable of forming onium compounds (O and N), and also by the possibility of the formation of a hydrogen bond [3].

In order to extend our ideas concerning the properties of 2-vinyloxyethylamine, in the present investigation, we have studied its behavior in polymerization and copolymerization reactions proceeding by a free-radical mechanism. Investigations in this direction have been made for alkyl vinyl ethers [4, 5, 6], but there have been none at all for vinyl ethers containing functional groups (NH_2 or OH).

Experiments on the polymerization of 2-vinyloxyethylamine showed that, as in the case of alkyl vinyl ethers [4, 5], polymerization could not be induced by benzoyl peroxide. Hence, a component was selected for copolymerization with 2-vinyloxyethylamine which is known to react by a free-radical mechanism in presence of benzoyl peroxide and could draw the double bond of the vinyl ether into the process. As a result of this investigation, the copolymerization of 2-vinyloxyethylamine with methyl methacrylate was effected (Tables 1 and 2). The copolymers obtained contained various proportions of 2-vinyloxyethylamine, and these increased as the concentration of the vinyl ether in the original mixture was increased.

TABLE 1

Expt. No.	Molar ratio of vinyl ether to methyl methacrylate	Yield of reaction products		Extent to which methyl methacrylate participated in copolymerization (%)
		copolymer (% of total amount)	addition product (% of theoretical)	
1	0:1	94	—	94.0
2	1:19	6	74.5	6.3
3	1:3	24	50.5	29.9
4	1:1	34	44.1	57.0
5	3:1	18	50.0	50.5
6	19:1	4	55.5	54.5
7	1:0	Does not polymerize	—	—

On the basis of considerations that we have advanced previously [4], the mechanism of the copolymerization process can be visualized as follows: the benzoyl peroxide initiates a molecule of methyl methacrylate with formation of an active radical, which then draws the double bond of the 2-vinyloxyethylamine into the chain reaction. This is confirmed by the absence of polymerization in pure 2-vinyloxyethylamine in presence of benzoyl peroxide under these con-

ditions; methyl methacrylate, on the other hand, owing to the presence of conjugated bonds $-\text{C}=\text{C}-\text{C}=\text{O}$, is very active in these processes.

Nevertheless, it must be emphasized that in the present case, no methyl methacrylate polymer was found among the reaction products. It has thus been shown that copolymerization is not accompanied by formation of the polymer of the initially active component. It has been established, however, that reaction of 2-vinyloxyethylamine with methyl methacrylate proceeds not only with formation of copolymers, but with formation also of the methyl ester of 2-methyl-3-(2-vinyloxyethylamino) propionic acid in accordance with the equation:

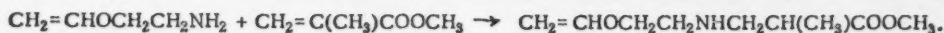


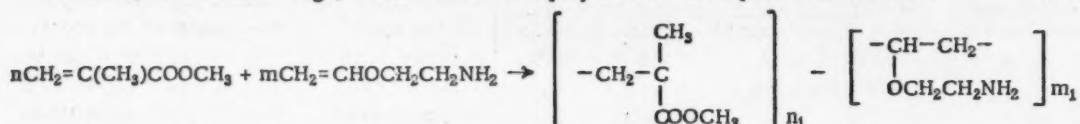
TABLE 2

Expt. No.	Molar ratio of vinyl ether to methyl methacrylate	Nitrogen content of copolymer (%)	Molar content of vinyl ether in copolymer (%)	Molar ratio of vinyl ether to methyl methacrylate in copolymer	Relative viscosity η_{rel}	Description of polymer or copolymer
1	0:1	—	—	0:1	3.61	Colorless, hard, brittle, soluble in acetone
2	1:19	0.25	1.8	1:55	1.297	The same
3	1:3	0.5 0.6	3.9	1:24.5	2.54	The same
4	1:1	1.77 1.73	12.4	1:7.0	—	Colorless, hard, insoluble in usual solvents; does not melt
5	3:1	4.30 4.11	29.0	1:2.5	—	Yellow, hard, insoluble in usual solvents
6	19:1	5.07 5.33	35.7	1:2.0	—	The same

It has been shown that benzoyl peroxide is without effect on the course of this reaction: methyl 2-methyl-3-(2-vinyloxyethylamino) propionate is formed in the same yield, both in presence and absence of benzoyl peroxide. Under the given conditions the yield of product depends on the ratio of the original components: it increases with increase in the excess of methyl methacrylate (Table 3).

Investigation of the properties of methyl 2-methyl-3-(2-vinyloxyethylamino)propionate has shown that under the given conditions it not only does not polymerize in presence of benzoyl peroxide, but also does not copolymerize with methyl methacrylate. The possibility of this product being involved in the chain polymerization reaction is, therefore, apparently excluded.

Hence, in the initial stage, the formation of copolymers can be represented as follows:



Cross-linking with formation of a three-dimensional structure then follows, and infusible, insoluble copolymers result. In the present case, the cross-linking of the macromolecules may proceed with the participation of the functional groups NH_2 , COOCH_3 , and $\text{CH}_2=\text{C}(\text{CH}_3)$, leading to the formation of linkages of the type

$\text{—}\overset{\text{O}}{\parallel}\text{C—NH—}$ or $\text{—NH—CH}_2\text{—CH}(\text{CH}_3)\text{—}$. This is confirmed by 1) the fact that methyl 2-methyl-3-(2-vinyloxyethylamino)propionate is formed, and 2) data in the literature on the reactions of acrylic acid derivatives with amines [7-10].

EXPERIMENTAL

A. Starting materials. 2-Vinyloxyethylamine was purified by treatment with sodium followed by distillation: b.p. 115-117°; n_D^{20} 1.4390. The methyl methacrylate used had the following constants: b.p. 34.5° (55 mm); n_D^{20} 1.4150. The benzoyl peroxide was purified by being precipitated twice from chloroform solution with methanol; it contained 99.1% of the peroxide.

B. Experimental procedure. Copolymerization was carried out in glass tubes, which were heated in a thermostat at 60-62°. The starting materials (5 g in all) were taken in various molar ratios, and 0.01 g of benzoyl peroxide was added (0.2% on the total amount of monomers). The process was continuous over 100 hours. Under the same conditions two control experiments were performed on the polymerization in presence of benzoyl peroxide of pure methyl methacrylate and pure 2-vinyloxyethylamine. The treatment of the reaction products was determined by their properties.

I. Copolymerization of 2-Vinyloxyethylamine and Methyl Methacrylate

a) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 1:19. At the end of 100 hours, the mixture obtained from 0.22 g of 2-vinyloxyethylamine and 4.67 g of methyl methacrylate remained liquid; 4.9 g of it was vacuum distilled and yielded the following fractions:

Fraction I, b.p. 18° (10 mm); n_D^{20} 1.4155; 3.9 g

Fraction II, viscous residue $\frac{1.0 \text{ g}}{4.9 \text{ g}}$

Fraction I was methyl methacrylate. Fraction II was dissolved in acetone, from which it was precipitated as a white solid by means of methanol; this solid was separated from the main solution and vacuum-dried at 20°, yielding 0.3 g of a hard brittle colorless polymer. For the purpose of analysis, it was twice precipitated from acetone solution with methanol.

Found %: C 59.89; 59.64; H 8.37; 8.18; N 0.25

The analysis corresponded to a copolymer containing traces of nitrogen.

The acetone-methanol solution was vacuum-distilled, and yielded:

Fraction I, b.p. 120-125° (20 mm); n_D^{20} 1.4499; 0.35 g

Fraction II, resin $\frac{0.05 \text{ g}}{0.40 \text{ g}}$

Fraction I was methyl 2-methyl-3-(2-vinyloxyethylamino)propionate. The detailed investigation of this fraction is given in g) (below).

b) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 19:1. Throughout the whole course of the polymerization process the reaction mixture remained liquid. Its treatment was carried out as in the preceding experiment, with the exception that the copolymer was purified not by the precipitation method, but by repeated washing with acetone. No methyl methacrylate polymer could be detected in the acetone washings.

c) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 1:3. Thirty hours after the commencement of the heating of 1.12 g of 2-vinyloxyethylamine with 3.88 g of methyl methacrylate, a rise in viscosity was observed. Toward the end of the process the reaction product became very thick, but was still fluid. It was dissolved in acetone, from which it was precipitated by methanol as a hard, brittle, colorless polymer (1.2 g). Before analysis, the polymer was washed repeatedly with methanol.

Found %: C 59.98; 59.99; H 8.20; 8.22; N 0.5; 0.6

The analysis corresponded to a copolymer containing 3.9 mole-% of the vinyl ether.

Vacuum distillation of the alcohol-acetone solution yielded:

Fraction I, b.p. 125-130° (25 mm); n_D^{20} 1.4491; 1.3 g

Fraction II, resin $\frac{0.1 \text{ g}}{1.4 \text{ g}}$

The investigation of Fraction I, which was methyl 2-methyl-3-(2-vinyloxyethylamino)propionate, is described under g).

d) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 3:1. During the polymerization process the viscosity varied as in c). The product, however, was insoluble in most solvents (acetone, ether, benzene, alcohols, water, dioxane, vinyl ethers, chloroform, etc.) and was, therefore, purified by repeated washing with acetone and ether. No methyl methacrylate polymer was isolated from the acetone-ether mixture.

e) Copolymerization at a molar ratio of 2-vinyloxyethylamine to methyl methacrylate of 1:1. Polymerization began after six hours, and attained a maximum after 43 hours. The reaction product was a jellylike substance and was treated as in d). No methyl methacrylate polymer was obtained.

f) Polymerization of pure methyl methacrylate. Under the conditions described under B, methyl methacrylate polymerized to a solid in six hours, but it was kept in the thermostat for 100 hours in order to give comparable results. The product was dissolved in acetone, from which it was precipitated by methanol as a hard, brittle, colorless polymer.

The results of all of the copolymerization experiments are given in Tables 1 and 2.

g) Investigation of the product accompanying the copolymer. The product was collected from all of the experiments on the copolymerization of 2-vinyloxyethylamine and methyl methacrylate, and was vacuum-distilled. In its analysis it corresponded to the compound:



It was a colorless liquid, soluble in benzene, ether, acetone, and methanol, having b.p. 97.5° (4 mm); n_D^{20} 1.4491; d_4^{20} 0.9998; calculated for $\text{C}_9\text{H}_{17}\text{O}_3\text{N}$ MR 50.19; found MR 50.24; found (cryoscopically in benzene) M 182.0; 178.2; calculated for $\text{C}_9\text{H}_{17}\text{O}_3\text{N}$ M 187.2.

	Found %	C 57.75; 57.97;	H 9.27; 9.19;	N 7.51; 7.61
$\text{C}_9\text{H}_{17}\text{O}_3\text{N}$.	Calculated %	C 57.80;	H 9.12;	N 7.50

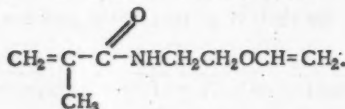
Hydrogenation of the product over Raney nickel at 56° in an autoclave yielded methyl 3-(2-ethoxyethyl-amino)-2-methylpropionate: b.p. 82° (2 mm); n_D^{20} 1.4333; d_4^{20} 0.9668; MR 50.88; calculated for $\text{C}_9\text{H}_{19}\text{O}_3\text{N}$ MR 50.54.

	Found %	C 57.25; 56.99;	H 10.24; 10.10;	N 7.47; 7.45
$\text{C}_9\text{H}_{19}\text{O}_3\text{N}$.	Calculated %	C 57.26;	H 10.12;	N 7.40

Other facts confirming the structure of the product are:

1. The ease and completeness of its hydrolysis by 2% sulfuric acid, which indicates presence of a vinyl group. The acetaldehyde formed in this way was determined iodometrically [11], giving, for the content of the compound, 96.3, 96.9%.

2. A negative reaction for the $-\text{C}(=\text{O})\text{NH}-$ grouping, which would be present if the compound formed in the reaction was



3. The compound did not polymerize in presence of benzoyl peroxide, which indicates the absence of a double bond capable of entering into polymerization by a radical mechanism under the given conditions.

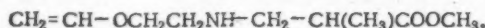
4. The participation of the amino group of 2-vinyloxyethylamine in the formation of the compound under consideration was confirmed by the fact that N,N-diethyl-2-vinyloxyethylamine C_2H_5 $\text{N}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{OCH}=\text{CH}_2$ did not yield a similar compound with methyl methacrylate.

II. Reaction of 2-Vinyloxyethylamine with Methyl Methacrylate when Heated in Absence of Benzoyl Peroxide

A mixture of 2.33 g of 2-vinyloxyethylamine and 2.67 g of methyl methacrylate was heated in a thermostat under the conditions described under B. The reaction product was vacuum distilled, and yielded:

Fraction I, b.p. 27-32° (29 mm); n_D^{20} 1.4256;	2.7 g
Fraction II, b.p. 132.5° (24 mm); n_D^{20} 1.4493;	2.2 g
Fraction III, resin	$\frac{0.05 \text{ g}}{4.95 \text{ g}}$

Fraction I was a mixture of the starting materials. Fraction II corresponded to the addition product formed by 2-vinyloxyethylamine and methyl methacrylate:



Experiments were carried out in similar fashion in which molar ratios of vinyl ether to methyl methacrylate of 1:19 and 19:1 were used. The results are given in Table 3.

TABLE 3

Expt. No.	Molar ratio of 2-vinyl-oxyethylamine to methyl methacrylate	Yield of addition product (% of theoretical)
1	1:19	85.2
2	1:1	43.2
3	19:1	59.3

SUMMARY

1. It has been shown that pure 2-vinyloxyethylamine does not polymerize in presence of benzoyl peroxide under the conditions used.

2. The copolymerization of 2-vinyloxyethylamine and methyl methacrylate has been effected in presence of benzoyl peroxide.

3. It has been shown that, together with copolymerization, the formation of a new substance, methyl 2-methyl-3-(2-vinyloxyethylamino)propionate, occurs.

4. It has been pointed out that, in the course of the formation of the macromolecular compounds, not only double bonds, but also other functional groups of the original components, take part in the reaction.

5. Polymers of methyl methacrylate were absent in the reaction products.

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** See Consultants Bureau Translation, page 335.

*** See Consultants Bureau Translation, page 931.

STEROCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 3. *cis*- AND *trans*-4-CYCLOHEXENE-1,2-DICARBOXYLIC ACIDS, AND THEIR REACTIONS

I. N. Nazarov and V. F. Kucherov

When Diels and Alder in 1928 prepared *cis*-4-cyclohexene-1,2-dicarboxylic acid by the condensation of maleic anhydride with 1,3-butadiene [1], it became clear that the structures of various cyclohexene-1,2-dicarboxylic acids and their derivatives; described previously by Bayer [2], did not correspond to the formulas ascribed to them. This is particularly true of the compounds of the *trans* series.

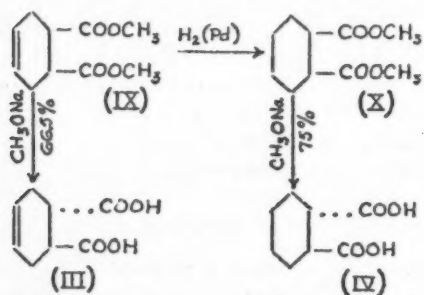
It was not till 1948 that Korolev and Mur [3] described for the first time the preparation of *trans*-4-cyclohexene-1,2-dicarboxylic acid by the condensation of 1,3-butadiene with fumaric acid and its acid chloride in boiling acetic acid. Shortly afterwards Alder and Schumacher [4], while studying the stereochemistry of the diene synthesis, also obtained this *trans*-acid and cleared up the question of the structures of various cyclohexene-1,2-dicarboxylic acids obtained by Bayer from the reduction of phthalic acid [2]. Quite recently, *trans*-4-cyclohexene-1,2-dicarboxylic acid has been prepared in 55% yield by heating 1,3-butadiene with fumaric acid in aqueous solution at 135° [5].

Having developed a convenient method for the synthesis of cyclic *trans*-1,2-dicarboxylic acids by the condensation of dienes with *trans*-dienophiles [6], we have now applied it in the preparation of *trans*-4-cyclohexene-1,2-dicarboxylic acid (III) and its derivatives with the object of studying the stereochemical transformations in this series.

When a mixture of dimethyl fumarate and 5-6 molecular proportions of 1,3-butadiene was heated in benzene at 200-205°, a 95% yield (calculated on the fumaric ester) was obtained of the dimethyl ester of *trans*-4-cyclohexene-1,2-dicarboxylic acid (I), and this gave a dibromide of m.p. 85-86° which differed from that described by Bayer [2]. Hydrolysis of the *trans*-diester I readily gave the known *trans*-4-cyclohexene-1,2-dicarboxylic acid (III), m.p. 171-172°, and hydrogenation of the ester gave the saturated *trans*-diester II, readily hydrolyzable to the known *trans*-1,2-cyclohexanedicarboxylic acid (IV).

When the *trans*-acid III was heated with excess of acetyl chloride, the *trans*-anhydride V, m.p. 186-187°, described by Alder and Schumacher [4], was readily obtained, and this, when hydrogenated in chloroform in presence of a Pd catalyst, gave the saturated *trans*-anhydride VI, m.p. 145-146°, which could be readily prepared also by the action of acetyl chloride on the saturated *trans*-acid IV. Boiling of the *trans*-anhydride V in absolute methanol solution yielded the *trans*-monoester VII in quantitative yield, and this, on hydrogenation, gave the known saturated *trans*-monoester VIII, m.p. 96° [7].

The *trans*-acids III and IV can be readily prepared also by the isomerization and hydrolysis with sodium methoxide of the corresponding *cis*-diesters IX and X, which we prepared by the action of diazomethane on *cis*-4-cyclohexene-1,2-dicarboxylic acid and *cis*-1,2-cyclohexanedicarboxylic acid respectively:

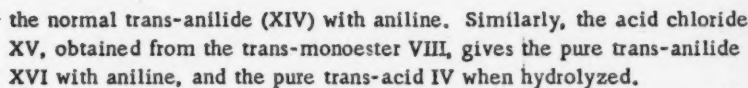


When the *trans*-anhydrides V and VI were heated at 200° for two hours, they were almost completely isomerized to the corresponding *cis*-anhydrides (XI and XII).

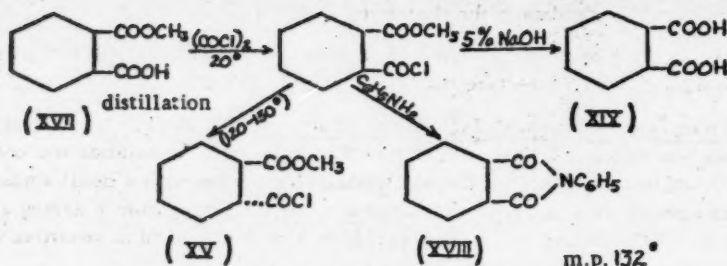
This fact points to the considerably lower stability of the *trans*-anhydrides V and VI to heat, as compared with the corresponding *trans*-anhydrides having an angular methyl group, which give, by thermal isomerization, an equilibrium mixture of *cis*- and *trans*-isomers, the latter predominating [6].

The corresponding *trans*-acids (III and IV) behave in the same way when heated.

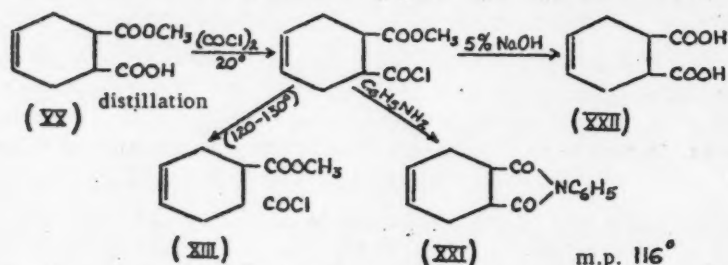
However, the acid chlorides prepared from the *trans*-monoesters VII and VIII are quite stable to heat. Thus the acid chloride XIII, obtained from the *trans*-monoester VII by the action of oxalyl chloride followed by distillation, is hydrolyzed quantitatively to the *trans*-acid III, and forms



This isomerization of the cis-acid chlorides takes place during their distillation, for these acid chlorides, when prepared from the pure cis-monoester XVII and XX and not distilled, give high yields of the cis-phenylimides when treated with aniline, and give the pure cis-acids XIX and XXII when hydrolyzed. This sort of



thermal isomerization of the cis form into the trans form in the preparation of acid chlorides has already been noted in a number of cases [8, 9], but it is almost absent in the case of cis-1-methyl-1,2-cyclohexanedicarboxylic and cis-1-methyl-4-cyclohexene-1,2-dicarboxylic acids, which we have studied previously [10].



EXPERIMENTAL

Dimethyl ester of trans-4-cyclohexene-1,2-dicarboxylic acid (I). A mixture of 15 g of dimethyl fumarate [12] 70 ml of absolute benzene, and 30 g of 1,3-butadiene was heated in a steel tube at 200-205° for 3 hours-30 minutes. The benzene was distilled off, and the residue was distilled under reduced pressure. Redistillation yielded 19.5 g of the trans-diester I as a mobile colorless liquid, b.p. 137° (20 mm); n_D^{20} 1.4650; d_4^{20} 1.1234; found MR 48.96; calculated MR 49.02.

	Found %	C 60.73; 60.45; H 7.27, 7.25
$\text{C}_{10}\text{H}_{14}\text{O}_4$	Calculated %	C 60.6; H 7.12

The dibromide: A chloroform solution of bromide was added in slight excess to a solution of 0.5 g of the trans-diester I in 10 ml of chloroform. The solvent was distilled off, and the crystalline product was crystallized twice from petroleum ether; m.p. 85-86°.

	Found %	Br 44.73; 44.79
$\text{C}_{10}\text{H}_{14}\text{O}_4\text{Br}_2$	Calculated %	Br 44.64

Dimethyl ester of trans-1,2-cyclohexanedicarboxylic acid (II). The trans-diester I (10 g), dissolved in 70 ml of absolute methanol, was hydrogenated in presence of a Pd catalyst at room temperature, 1.18 liter of hydrogen (one molecule) being absorbed. The methanol was distilled off, and the residue, when vacuum-distilled, yielded 9.6 g of the trans-diester II, b.p. 135° (17 mm); n_D^{20} 1.4524; d_4^{20} 1.0945; MR found 49.39; MR calculated 49.49.

	Found %	C 59.94; 59.92; H 7.99; 8.08
$\text{C}_{14}\text{H}_{16}\text{O}_4$	Calculated %	C 60.0; H 8.05

trans-4-Cyclohexene-1,2-dicarboxylic acid (III). A mixture of 10 g of the trans-diester I and 35 ml of a 20% solution of caustic potash was boiled for two hours, when solution was complete. The solution was mixed with charcoal and filtered. Acidification with hydrochloric acid yielded 7.9 g of the trans-acid III, m.p. 169-170°. After crystallization from 20% aqueous acetone the trans-acid melted at 171-172°, as given in the literature [3].

trans-1,2-Cyclohexanedicarboxylic acid (IV). a) A mixture of 5 g of the trans-diester II and 20 ml of a 20% solution of caustic potash was boiled for two hours, when solution was complete. Acidification of the solution yielded 4.1 g of the trans-acid IV, m.p. 214-216°. After crystallization from 20% acetone it melted at 218-220° (with decomposition), which corresponds to the data in the literature.

b) Hydrogenation of 1 g of the trans-acid III in absolute methanol in presence of a Pd catalyst yielded, after crystallization from water, 0.67 g of the pure trans acid IV, m.p. 217-219° (with decomposition).

Anhydride of trans-4-cyclohexene-1,2-dicarboxylic acid (V). A mixture of 7.5 g of the trans-acid III and 80 ml of acetyl chloride was boiled in a flask under reflux for two hours, when solution was complete. The acetyl chloride was distilled off, and the crystalline residue was washed on the filter with a small amount of petroleum ether. Two crystallizations from absolute ethyl acetate yielded 4.8 g of the trans-anhydride V having a constant m.p. of 188-189°, as given in the literature [4]. Boiling of the trans-anhydride V with water led to quantitative recovery of the trans-acid III.

Anhydride of trans-1,2-cyclohexanedicarboxylic acid (VI). The trans-anhydride V (0.8 g), dissolved in 30 ml of chloroform, was hydrogenated in presence of a Pd catalyst, 180 ml of hydrogen (one molecule) being absorbed. The solvent was distilled off, and the crystalline product was washed on the filter with a mixture of benzene and absolute ether (4:1). After crystallization from a mixture of benzene and ether, the trans-anhydride obtained (VI, 0.45 g) melted at 145-146°. The same trans-anhydride (VI) was readily obtained by the action of acetyl chloride on the trans-acid IV. According to the literature [2], the trans-anhydride VI melts at 140°.

Monomethyl ester of trans-4-cyclohexene-1,2-dicarboxylic acid (VII). A solution of 3 g of the trans-anhydride V in 30 ml of absolute methanol was boiled for two hours, and the solvent was then distilled off under reduced pressure. The residual liquid readily crystallized out when petroleum ether was added, and 2.8 g of the trans-monoester VII was obtained. Its melting point after two crystallizations from a mixture of benzene and petroleum ether (1:4) was 58-59°.

	Found %:	C 58.45; 58.39;	H 6.54; 6.33
$C_9H_{12}O_4$	Calculated %:	C 58.68;	H 6.57

Monomethyl ester of trans-1,2-cyclohexanedicarboxylic acid (VIII). The trans-monoester VII (0.5 g), dissolved in 10 ml of benzene, was hydrogenated over a Pd catalyst. When one molecule of hydrogen had been absorbed, the solvent was distilled off. Treatment of the liquid residue with petroleum ether yielded a crystalline product (0.44 g) of m.p. 93-94.5° (the trans-monoester VIII), which melted, after recrystallization from a mixture of benzene and petroleum ether (1:5), at 95-96°, as given in the literature [7]. The same trans-monoester (m.p. 94-95°) was obtained when the trans-anhydride VI was boiled in absolute methanol.

Monomethyl ester of cis-4-cyclohexene-1,2-dicarboxylic acid (XX). A solution of 40 g of the anhydride of cis-4-cyclohexene-1,2-dicarboxylic acid [1] in 350 ml of absolute methanol was boiled for three hours. Methanol was distilled off under reduced pressure, and the liquid residue rapidly crystallized out on addition of petroleum ether, yielding 42.7 g of the cis-monoester XX, m.p. 74-76°. After two crystallizations from a mixture of absolute ether and petroleum ether (1:2), the cis-monoester had a constant melting point of 84-85°.

	Found %:	C 58.28; 58.30;	H 6.50; 6.49
$C_9H_{12}O_4$	Calculated %:	C 58.68;	H 6.56

Hydrogenation of the cis-monoester XX in methanol in presence of a Pd catalyst yielded the saturated cis-monoester XVII, m.p. 68-69°, identical with the substance described in the literature [11].

Dimethyl ester of cis-4-cyclohexene-1,2-dicarboxylic acid (IX). A suspension of 5 g of cis-4-cyclohexene-1,2-dicarboxylic acid [1] in 50 ml of ether was treated with an ethereal solution of diazomethane. After removal of solvent, the residue was distilled, and yielded 4.9 g of the cis-diester IX, b.p. 114-115° (5 mm); n_D^{20} 1.4728.

	Found %:	C 60.42; 60.54;	H 7.05; 7.34
$C_{10}H_{14}O_4$	Calculated %:	C 60.6	H 7.12

Dimethyl ester of cis-1,2-cyclohexanedicarboxylic acid (X). Similar treatment of cis-1,2-cyclohexanedicarboxylic acid with diazomethane yielded the cis-diester X, b.p. 110-111° (5 mm); n_D^{20} 1.4590.

	Found %:	C 59.72; 59.72;	H 7.91; 7.87
$C_{10}H_{16}O_4$	Calculated %:	C 60.0;	H 8.05

The same ester was prepared also by hydrogenation of the cis-diester IX in methanol in presence of a Pd catalyst.

Isomerization of the cis-diester IX. A solution of sodium methoxide was prepared from 7.5 g of sodium and 180 ml of absolute methanol, 2.8 g of the cis-diester IX was added, and the mixture was boiled for 15 hours. Methanol was distilled off under reduced pressure, and the residue was dissolved in a small amount of water. The solution was treated with charcoal, filtered, and acidified, when it yielded 1.6 g (66.5%) of trans-4-cyclohexene-1,2-dicarboxylic acid (III), m.p. 170-171°, undepressed by admixture with an authentic sample.

Isomerization of the cis-diester X. The procedure was as in the preceding experiment: from 3 g of the diester X a 75% yield was obtained of pure trans-1,2-cyclohexanedicarboxylic acid, m.p. 218-220° and identical with the sample prepared previously.

Isomerization of the trans-anhydride V. The trans-anhydride V (1 g; m.p. 186-188°) was heated in a flask under reflux for two hours at 200°. When cool, the liquid product crystallized out, and yielded 0.9 g of a yellow crystalline substance, which was recrystallized from benzene. The product (0.8 g) melted at 102-103°, undepressed by admixture with a pure sample of the cis-anhydride XI.

Isomerization of the trans-anhydride VI. The trans-anhydride VI (1 g; m.p. 144-145°) was heated for two hours at 200-205°. Hydrolysis of the colored liquid product was effected by boiling it with 4 ml of water until solution was complete, and the solution, when cool, yielded 0.75 g of pure cis-1,2-cyclohexanedicarboxylic acid (XIX), m.p. 189-190°, undepressed by admixture with an authentic sample.

Acid chloride of the trans-monoester VII (XIII). Oxalyl chloride (2 ml) was added to a solution of 2 g of the trans-monoester VII in 20 ml of absolute benzene, and the resulting solution was set aside for three hours at room temperature. Benzene was distilled off, and the liquid residue was vacuum-distilled, yielding 1.9 g of the acid chloride XIII, b.p. 112-112.5° (6 mm); n_D^{20} 1.4870.

Found %: Cl 17.85; 17.95
 $C_9H_{11}O_3Cl$. Calculated %: Cl 17.51

The acid chloride XIII (0.7 g) was hydrolyzed at the boil with 10 ml of 10% caustic soda (10 minutes). On acidification 0.6 g of the trans-acid III, m.p. 170-172°, separated.

The trans-anilide XIV. A solution of 1 g of aniline in 10 ml of absolute ether was added slowly to a cooled (to 0°) solution of 1 g of the acid chloride XIII in 30 ml of absolute ether. The mixture was allowed to stand for one hour at room temperature and then treated with water. The ether layer was separated, washed successively with 5% hydrochloric acid, 5% caustic soda solution, and water, and finally dried over sodium sulfate. The ether was distilled off, and the crystalline residue was washed on the filter with a mixture of ether and petroleum ether (1:1). The product was 1.1 g of the trans-anilide XIV, m.p. 134-136°. After crystallization from 70% aqueous methanol it melted at 136-137°.

Found %: C 69.62; 69.41; H 6.53; 6.55; N 5.78; 5.64
 $C_{15}H_{17}O_3N$. Calculated %: C 69.48; H 6.68; N 5.40

Acid chloride of the trans-monoester VIII (XV). By the procedure used for the acid chloride XIII, 2 g of the trans-monoester VIII yielded, after distillation, 1.8 g of the acid chloride XV, b.p. 114.5-115° (7 mm); n_D^{20} 1.4750.

Found %: Cl 17.49; 17.64
 $C_9H_{13}O_3Cl$. Calculated %: Cl 17.33

On hydrolysis with 10% caustic soda solution, 0.7 g of the acid chloride XV yielded 0.65 g of trans-1,2-cyclohexanedicarboxylic acid (IV), m.p. 218-220°.

The trans-anilide XVI. By the usual procedure, 1 g of the acid chloride XV in ether solution yielded 1.15 g of the anilide, m.p. 123-124°. After recrystallization from 60% methanol the trans-anilide XVI had a constant m.p. of 126-127.5°.

Found %: C 69.25; 69.21; H 7.27; 7.24; N 5.47; 5.50
 $C_{15}H_{19}O_3N$. Calculated %: C 68.96; H 7.33; N 5.36

The cis-phenylimide XVIII. Oxalyl chloride (1 ml) was added to a solution of 1 g of the cis-monoester XVII in 10 ml of absolute benzene, and the resulting solution was set aside for two hours at room temperature. Solvent was removed under reduced pressure (at 35-40°), and the residue was dissolved in 30 ml of absolute ether. The solution was cooled to 0° and stirred while a solution of 1 g of aniline in 10 ml of absolute ether was added slowly. The reaction product was allowed to stand for one hour at 0° and then treated as in the preceding experiment. The ether was driven off, and the crystalline product was washed on the filter with a mixture of ether and petroleum ether (1:1).

yielding 0.85 g of a substance of m.p. 120-126°. After recrystallization from 50% methanol, the *cis*-phenylimide XVIII melted at 132-133°.

Found %: C 73.53; 73.51; H 6.70; 6.83

$C_{14}H_{15}O_2N$. Calculated %: C 73.3; H 6.6

The *cis*-phenylimide XXI. By the procedure of the preceding experiment, 1 g of the *cis*-monoester XX was converted into the acid chloride, which, without being distilled, was caused to react with aniline, and yielded 0.75 g of the *cis*-phenylimide XXI, m.p. 115-116° (from 70% methanol).

Found %: N 6.31; 6.34

$C_{14}H_{15}O_2N$. Calculated %: N 6.16

Reactions of the acid chloride of the *cis*-monoester XVII. a) Oxalyl chloride (5 ml) was added to a solution of 5 g of the *cis*-monoester XVII in 50 ml of absolute benzene, and the resulting solution was set aside for two hours at room temperature. After removal of solvent under reduced pressure (30-35°), a liquid acid chloride remained.

Part of this acid chloride (0.5 g), without being distilled, was hydrolyzed at the boil with 7 ml of 5% caustic soda for five minutes. Acidification of the solution yielded 0.4 g of the *cis*-acid XIX, m.p. 191-192°, undepressed by admixture with an authentic sample (190-191°).

b) The remaining liquid acid chloride was vacuum-distilled, and yielded 4 g of a substance of b.p. 113-114° (5 mm) and n_D^{20} 1.4740. A portion (2 g) of the distilled acid chloride was hydrolyzed at the boil with 30 ml of 5% caustic soda for 10 minutes. Acidification yielded 1.8 g of an acid, m.p. 195-205°. This substance was recrystallized from water containing a little acetone, and 1.5 g of crystals of m.p. 200-212° was obtained. Recrystallization from 30% acetone yielded 0.8 g of the *trans*-acid IV, m.p. 218-220°, undepressed by admixture with an authentic sample. Fractional crystallization from water, applied to the mother liquors from the separation of the *trans*-acid IV, yielded 0.4 g of the *cis*-acid XIX, m.p. 189-191°.

c) The anilide was prepared by the usual method from 1 g of the distilled acid chloride. After removal of ether, 0.95 g of a crystalline substance of m.p. 95-110° was obtained. This substance was treated with warm ether, and the insoluble residue (0.5 g) melted, after crystallization from 60% methanol, at 126-127°, and gave no depression in admixture with the pure *trans*-anilide XIV. A heterogeneous crystalline product was obtained from the ether solution, and from this, by fractional crystallization, first from ether and then from 50% methanol, 0.2 g of another crystalline substance was isolated in the form of long fine needles, m.p. 100-102°. The analysis of this substance corresponded to an equimolecular mixture of the *trans*-anilide XIV and the *cis*-phenylimide XVIII. An artificially prepared mixture of XIV and XVIII melted, after crystallization from 50% methanol, at 100-102°, and showed no melting point depression in admixture with our second crystalline product of m.p. 100-102°.

Reactions of the acid chloride of the *cis*-monoester XX. a) The *cis*-monoester XX (5 g) was converted by the usual method into its acid chloride, and 0.5 g of this acid chloride, without being distilled, was hydrolyzed with 5% caustic soda. The product was 0.35 g of the *cis*-acid XXII, m.p. 166-167°, undepressed by admixture with a known sample.

b) Vacuum distillation of the remaining acid chloride yielded 3.8 g of acid chloride of b.p. 118-119° (7 mm) and n_D^{20} 1.4865. A portion (2 g) of this acid chloride was hydrolyzed in the usual way with 5% caustic soda, and 1.7 g of a mixture of acids was isolated. The mixture had a wide melting range (150-160°), and attempts to separate it by crystallization were not successful.

c) From 0.5 g of the distilled acid chloride, by treatment with aniline (0.5 g) in the usual way, 0.4 g of a crystalline substance of m.p. 95-120° was obtained. The residue (0.22 g) remaining after treatment with boiling ether melted at 132-135°, and this, when crystallized from 60% methanol, yielded 0.15 g of the pure *trans*-anilide XIV, m.p. 135-136°. The residue from the evaporation of the ether solution was crystallized from ether and from 50% methanol, and 0.1 g of a substance of m.p. 96-98° was isolated. This second crystalline product was found to be identical with an artificial mixture of equal amounts of the *trans*-anilide XIV and the *cis*-phenylimide XXI.

SUMMARY

1. 1,3-Butadiene has been condensed with methyl fumarate to give the dimethyl ester of *trans*-4-cyclohexene-1,2-dicarboxylic acid (I) in excellent yield. A number of derivatives of *cis*- and *trans*-4-cyclohexene-1,2-dicarboxylic acids have been prepared.

2. By the action of sodium methoxide, the isomerization of the *cis*-esters IX and X has been effected, the corresponding acids of the *trans* series (III and V) being obtained in good yield. It has been shown that at 200° the

trans-anhydrides V and VI are quantitatively isomerized to the corresponding cis-anhydrides (XI and XII).

3. Investigation has shown beyond doubt that the acid chlorides prepared from the cis-monoesters XVII and XX undergo thermal isomerization into the corresponding trans-acid chlorides, a process that occurs during distillation.

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• See Consultants Bureau Translation, page 301.

•• See Consultants Bureau Translation, page 51.

HYDROGENATION AND DEHYDROGENATION OF HYDROCARBONS IN PRESENCE OF RUTHENIUM AND RHODIUM CATALYSTS OF LOW METAL CONTENT

Kh. M. Minachev, N. I. Shuikin, and I. D. Rozhdestvenskaya

Ruthenium and rhodium catalysts have received very little application in hydrogenation and dehydrogenation catalysis. This fact is to be explained first by the extreme rarity of these metals in nature, and second by their almost complete insolubility, not only in the usual acids, but also in aqua regia. The preparation of their salts and oxides is, therefore, associated with considerable difficulties. Apart from this, there are indications in the literature that ruthenium supported by asbestos or active charcoal has a vigorous decomposing effect on cyclohexane, without effecting any appreciable dehydrogenation. Thus, Zelinsky and Turova-Polyak [1] in experiments on the dehydrogenation of cyclohexane in presence of a 30% ruthenium catalyst (on asbestos) found that this catalyst begins to dehydrogenate cyclohexane already at 250°, but the benzene formed, even under these mild conditions, was broken down to methane. Similar results were obtained by Borisov and Stepanov [2] in the dehydrogenation of cyclohexane in presence of a 30% ruthenium catalyst (on active charcoal). Rhodium catalysts, judging from the results of the same exploratory investigations, do not have any great tendency to induce scission, but their dehydrogenating propensity has received insufficient study. In the investigations cited it is shown that ruthenium and rhodium catalysts are very efficient for the hydrogenation of the benzene ring.

Fischer, Bahr, and Meusel [3] have used metallic ruthenium and finely dispersed ruthenium on asbestos (metal content 35%) in the catalytic reduction of carbon dioxide to methane and higher hydrocarbons (at 125-150°). The authors state that the catalysts become more active when given a preliminary treatment for two hours with air at 300-400°, with 5% nitric acid, or with potassium or rubidium carbonate.

Kiperman [4] showed that the activation energy for the decomposition of ammonia at a Ru/silica gel catalyst is 59,950 cal/mole, whereas for the same reaction at vanadium and osmium catalysts he found 45,000 cal/mole. The author ascribes this difference to the high hydrogen adsorption at a ruthenium surface.

Dunworth and Nord [5] have recently used 5% rhodium on active charcoal in the reduction of aromatic and aliphatic nitro compounds, and also for the hydrogenation of carbon-carbon double bonds in various fatty acids. The authors showed that a nitro group in a benzene ring is reduced much more rapidly than the nitro group of an aliphatic compound. The carbon-carbon double bond in fatty acids is hydrogenated smoothly, but considerably more slowly with this catalyst than with colloidal rhodium supported on polyvinyl alcohol [6].

In our previous communications [7] we have described the hydrogenation and dehydrogenation properties of platinum, palladium, nickel, and cobalt catalysts in their relation to the ratio of metal to carrier. It was shown that these catalysts could be successfully used for the hydrogenation and dehydrogenation of hydrocarbons. In the same investigations the structural peculiarities of platinum and palladium catalysts were characterized by X-ray analysis. It was shown that platinum retains its crystal structure on an amorphous carrier right down to the minimum concentration of 0.03%. On the basis of these results we made a suggestion concerning the way in which the metal is distributed on the surface of charcoal, and this was later confirmed by direct determinations.

Investigation of the structure of palladium catalysts showed that finely dispersed palladium on charcoal preserves its crystal structure right down to a metal concentration of 0.05%. It was shown by a study of the X-ray structures of Pt and Pd catalysts that had received prolonged exposure to the conditions of hydrogenation and dehydrogenation reactions that no recrystallization occurred under these conditions.

In continuation of our investigation of the specific characteristics of catalysts of low metal content, we have studied the hydrogenation and dehydrogenation properties of finely dispersed ruthenium and rhodium, supported on various carriers. Our interest was directed particularly to the following points: 1) the variation of the dehydrogenation activities of the catalysts with temperature; 2) the ability of these catalysts to bring about hydrogenation of the benzene ring, of cycloalkenes, and of alkenes; 3) the values of the activation energies for the dehydrogenation of cyclohexane over these catalysts; and 4) the elucidation of the structural peculiarities of these catalysts.

EXPERIMENTAL

Preparation of catalysts. Four catalysts were prepared: 1) 1% Ru on aluminum oxide; 2) 1% Ru on active charcoal; 3) 1% Rh on aluminum oxide; and 4) 1% Rh on active charcoal. The rhodium catalysts were prepared by impregnation of the corresponding carriers with a solution of H_2RhCl_6 at room temperature, and the ruthenium catalysts were prepared under the same conditions from a solution of NH_4RuCl_5NO .

Procedure. The catalysts, after being dried at 120° , were reduced with electrolytic hydrogen directly in the reaction tube at $325-330^\circ$. The experiments on the hydrogenation and dehydrogenation of hydrocarbons were carried out in the usual continuous-flow apparatus, as described previously [7]. In all cases, the volume of reduced catalyst was 50 ml. The conversion of cyclohexane into benzene, and of benzene into cyclohexane, was followed refractometrically [8]. The gas analysis was carried out in the usual VTI gas analyzer.

Experimental Results

The extent to which cyclohexane is dehydrogenated over these catalysts is shown for various temperatures in Table 1 (the space velocity for the passage of cyclohexane was 0.3 liter per liter of catalyst per hour). As will be seen from Table 1, rhodium catalysts already have very high activity at 300° , and at $340-360^\circ$ the conversion of cyclohexane into benzene attains 92-95%. Ruthenium catalysts were found to be less active, even at elevated temperatures. The higher activity of the catalysts, both ruthenium and rhodium, on aluminum oxide is due to the fact that in the samples taken for investigation the metal content was three times as high as in the corresponding catalysts on charcoal. The essential difference between the catalysts studied by us and those studied in previous investigations [1, 2] is that they did not bring about scission of the cyclohexane ring below 300° . When cyclohexane was passed over these catalysts at $320-380^\circ$, the issuing gas contained 3.4-25.6% of methane hydrocarbons. This behavior in our catalysts is probably to be explained by the low metal content (as % of amount of carrier) and the considerable space velocity of the cyclohexane.

TABLE 1

Extent of Dehydrogenation of Cyclohexane over Rhodium and Ruthenium Catalysts at Various Temperatures

Catalyst	Temperature of experiment (°C)					Amount of metal in catalyst taken (g)
	300	320	340	360	380	
	Conversion of cyclohexane (%)					
Rh-charcoal.....	56	72	83	92	—	0.11
Rh-Al ₂ O ₃	76	84	95	—	—	0.30
Ru-charcoal.....	20.8	28.5	37.4	46.5	55	0.12
Ru-Al ₂ O ₃	28.5	34.8	43.6	52.8	67.4	0.30

Hydrogenation Properties of Rhodium and Ruthenium Catalysts

All four catalysts were very active in the hydrogenation of the benzene ring, and also of alkenes and cycloalkenes. The dependence of the degree of conversion of benzene on the space velocity is shown for rhodium-charcoal and ruthenium-charcoal catalysts in Fig. 1. As will be seen from this figure, the rhodium catalysts completely hydrogenated benzene at a space velocity of 0.13 liter per liter of catalyst per hour. With further increase in the

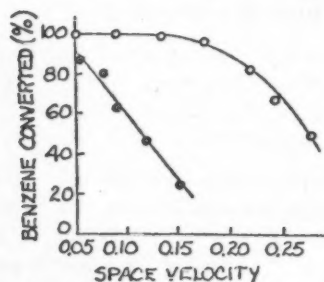


Fig. 1. Dependence of the degree of conversion of benzene on the space velocity at 150° : \circ = 1% Rh-charcoal; \square = 1% Ru-charcoal.

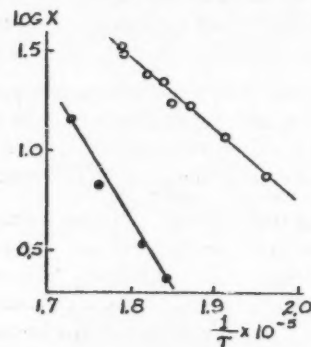


Fig. 2. Variation of the rate of dehydrogenation of cyclohexane with the temperature in presence of the catalyst: \circ = 1% Rh-charcoal; \square = 1% Ru-charcoal.

rate of passage of benzene, the percent conversion gradually falls, and at a space velocity of 0.28 it is 49. Under the same conditions the ruthenium catalyst promotes the hydrogenation of benzene in appreciably lower degree, but over the space velocity range of 0.05-0.07 liter of benzene per liter of catalyst per hour, the degree of conversion ranges correspondingly from 90 to 60%.

The results obtained for the hydrogenation of 1-methylcyclopentene and 1-octene are given in Table 2. These experiments were carried out at 140-143° at a space velocity of 0.11-0.12 liter per liter of catalyst per hour. The synthesis and properties of the hydrocarbons taken for hydrogenation have been described by us in a previous paper [7]. The results in Table 2 show that the properties of the hydrocarbons obtained are in close accord with those given in the literature [9, 10].

TABLE 2

Hydrogenation of Unsaturated Hydrocarbons over Rh-Charcoal and Ru-Charcoal Catalysts

Catalyst	Substance hydrogenated					
	1-methylcyclopentene			1-octene		
	Properties of Catalyzates					
	B.p. (°C)	n_D^{20}	d_4^{20}	B.p. (°C)	n_D^{20}	d_4^{20}
Rh-charcoal	71.4-72.2 (756 mm)	1.4102	0.7474	125.4-126 (758 mm)	1.3976	0.7072
Ru-charcoal	71.6-82.0 (757 mm)	1.4100	0.7471	125.4-126 (756 mm)	1.3972	0.7073

Kinetics of the Dehydrogenation of Cyclohexane over Rh-Charcoal and Ru-Charcoal Catalysts

No data exist in the literature on the kinetics of the dehydrogenation of cyclohexane over ruthenium and rhodium catalysts. We decided to determine the activation energies for these reactions and to compare the results with those for platinum and palladium catalysts. The experimental conditions were similar to those described in a previous paper [11]. The results are given in Table 3. Fig. 2 shows the variation of the rate of reaction with temperature, and it will be seen that the points give close fit to straight lines. This indicates that the variation in the rate of the dehydrogenation of cyclohexane with temperature obeys the Arrhenius law. The values of Q and K_0 found for the rhodium catalyst are fairly close to those for a palladium catalyst [12] ($Q = 15,800$ and $K_0 = 5,754 \cdot 10^5$) and are practically identical with those for platinum catalyst [11] ($Q = 15,250$ and $K_0 = 1.66 \cdot 10^5$). The values obtained for the ruthenium catalyst differ greatly from the values given by metal catalysts and approach the values obtained for the dehydrogenation of cyclohexane over chromium oxide [13].

This considerable difference between the activation energy for the dehydrogenation of cyclohexane over a ruthenium catalyst and that for the same reaction over other metal catalysts may be a result of a difference in crystal lattice. Ruthenium has a hexagonal lattice having the parameters $a = 2.695$ Å and $c = 5.273$ Å, whereas Pt,

TABLE 3

Kinetic Results on the Dehydrogenation of Cyclohexane in Presence of Ruthenium-Charcoal and Rhodium-Charcoal Catalysts

Catalyst	Expt. No.	Temp. (°C)	v_0 (in 10 min.)	Conversion (x, %)	$\log x$	$\frac{1}{T} \cdot 10^{-3}$	Activation energy Q , and pre-exponential term K_0
Rh-charcoal	1	285	372	33.7	1.5276	1.792	$Q = 16,800$ $K_0 = 1.44 \cdot 10^8$
	2	276	270.6	24.5	1.3892	1.821	
	3	260	193.6	17.5	1.2430	1.876	
	4	248	131.0	11.9	1.0755	1.919	
	5	236	84.4	7.6	0.8806	1.965	
	6	260	189.0	17.1	1.2330	1.876	
	7	270	250.6	22.8	1.3579	1.842	
	8	285	341.6	31.0	1.4914	1.792	
Ru-charcoal	1	277	42.0	3.5	0.5441	1.818	$Q = 30,200$ $K_0 = 1.77 \cdot 10^{13}$
	2	269	29.0	2.4	0.3802	1.845	
	3	294	80.2	6.8	0.8325	1.764	
	4	305	173	14.4	1.1584	1.730	

Pd, and Rh have cubic lattices. Also, according to data in the literature [14], ruthenium can sorb about 1520 volumes of hydrogen per unit volume of metal. Hence, the high activation energy for the dehydrogenation of cyclohexane over a ruthenium catalyst may be due to the high concentration of hydrogen at the surface of this catalyst.

X-ray Investigation of the Catalysts*

The catalyst samples were examined with chromium radiation of the K series ($\lambda = 2.285 \text{ \AA}$); exposure 12 hours at 10 milliamperes and 30 kv.

Ruthenium catalysts. Catalyst No. 1 (1% Ru on charcoal) gave only one weak line, corresponding to $d = 2.06 \text{ \AA}$; the discrepancy from the value given in tables (2.13 \AA) for the 110 line of Ru is probably to be explained by inaccuracy in the measurement of the line on the X-ray picture. Also, the possibility cannot be excluded that some deformation of the Ru lattice occurs under the influence of the carrier.

Catalyst No. 3 (1% Ru on Al_2O_3) gave a series of lines ($d = 2.12, 1.91$, and 1.37 \AA). The value of 2.12 corresponds to the 110 Ru lines, and $d = 1.91$ and 1.37 are characteristic lines of $\gamma\text{-Al}_2\text{O}_3$ ($hkl = 004$ and 044). In both cases the values were in agreement with those given in tables. The lattice parameters were calculated, with the following results:

Ru catalyst No. 1: $a = 2.690 \text{ \AA}$

Ru catalyst No. 3: $a = 2.697 \text{ \AA}$

The value given in reference tables is 2.697 \AA . Owing to the absence of other reflections, the parameter c was not determined. For $\gamma\text{-Al}_2\text{O}_3$ the value $a = 7.90 \text{ \AA}$ was obtained (tabular value 7.91 \AA).

Rhodium catalysts. Catalyst No. 2 (1% Rh on charcoal) gave only one weak line (Rh 111), very diffuse and difficult to measure ($d = 2.04 \text{ \AA}$; the tables give 2.20 \AA). Catalyst No. 4 (1% Rh on Al_2O_3) gave a weak Rh 111 line, $d = 2.14 \text{ \AA}$, and characteristic $\gamma\text{-Al}_2\text{O}_3$ lines ($d = 1.92$ and 1.38 \AA). For Rh catalyst No. 4 the value of a was found to be 3.74 \AA , and for Catalyst No. 2 the value 3.60 \AA was found (the tables give 3.79 \AA).

In Catalyst No. 4 $\gamma\text{-Al}_2\text{O}_3$ had a normal undeformed lattice. On all of the X-ray pictures the lines were very wide and diffuse, indicating a very high degree of dispersion (of the order of 10^{-7} cm) in the catalysts investigated.

SUMMARY

1. A study has been made of the hydrogenation and dehydrogenation propensities of rhodium and ruthenium catalysts supported on various carriers.
2. It has been shown that the activity of these catalysts for the hydrogenation of alkenes, cycloalkenes, and the benzene ring is close to that of a platinum catalyst.
3. The activation energies for the dehydrogenation of cyclohexane over ruthenium and rhodium catalysts have been determined.

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* The investigation of the X-ray structures of the catalysts was carried out by A. M. Rubinshtein, and we wish to express our thanks for this.

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INVESTIGATION BY THE ULTRACENTRIFUGE SEDIMENTATION METHOD OF THE MOLECULAR WEIGHT DISTRIBUTION FUNCTION OF POLYAMIDES

COMMUNICATION 1. DETERMINATION OF THE DISTRIBUTION FUNCTION OF POLYAMIDES FROM SEDIMENTATION CONSTANTS

S. I. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov

The study of the molecular weight distribution function of polymers presents a problem that has not yet been completely solved, in spite of its exceptionally high importance for the chemistry of macromolecular compounds. The extensively used laboratory method of fractional precipitation, followed by the construction of summative and differential molecular weight distribution curves from the fractionation data, contains errors that cannot be allowed for, since there always remains an unknown distribution function for each separate fraction. Theory and experiment show that, in the precipitation, the separating polymer fractions always carry with them a certain amount of substance belonging to all of the remaining fractions.

Recently, particularly in Svedberg's laboratory, the ultracentrifuge has been used in experiments on the determination of the distribution function of polymers. These investigations have shown the possibility, in principle, of solving our problem and have given us some idea of the molecular weight distribution of certain polymers (polystyrene, polymethylmethacrylate, and cellulose ethers and esters). The results of these investigations have been given in a review by Kinell and Ranby [1]. However, detailed examination of these results shows that the technique of the study of distribution functions and, in particular, the method used for the analysis of the experimental results cannot be regarded as completely satisfactory. In these experiments the polymer was fractionated by precipitation from solution, and each fraction was studied separately with the aid of the ultracentrifuge. The distribution function of each separate fraction was then treated arbitrarily as a triangle, the width of which was evaluated from the width of the experimental peak on the sedimentation diagram. Summation of the triangles corresponding to the separate fractions then led to the distribution function of the polymer with respect to sedimentation constants s , i.e., $\frac{dc}{ds} = f(s)$ (c is the concentration by weight, and s is the sedimentation constant). To pass from this function to the molecular weight distribution function characterizing the polymer $\frac{dc}{dM} = \varphi(M)$, it is necessary to make further, independent measurements (for example, of diffusion or of sedimentation equilibrium). With the exception of one old investigation (Signer and Gross) no such measurements have been carried out for any of the polymers.

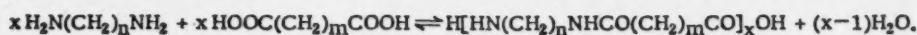
We must here point out a fundamental experimental difficulty in working with linear polymers: measurements of sedimentation and diffusion must be made at limiting dilutions so that the dependence of these values on concentration, which arises from the interaction of the macromolecules in solution, does not obscure the essential picture and can be taken into account in the form of a small correction (extrapolation to infinite dilution). The present refractometric methods used in ultracentrifuge experiments set a limit to the sensitivity of concentration measurements. Hence, a convenient subject for the study of the distribution function is provided by a linear polymer for which the degree of polymerization is not too high and the concentrational variations not too great at concentrations of 0.5-0.1% by weight.

In the present investigation, we selected mixed polyamides having molecular weights of up to 60,000. In this case, which is a simple one from the experimental point of view, we have succeeded in working out a method for determining the molecular weight distribution function that is free from any arbitrary element and contains no a priori assumptions.

We have retained the method, introduced by the Swedish workers, of preliminary fractionation followed by investigation of separate fractions. This increases the resolving power of the method, since the distribution function for each fraction is found to be a simple one. Experiment shows that it can be approximated very closely by a Gauss function. As a result, the quantitative analysis of the experimental results is considerably simplified. Also, such a method does not introduce any arbitrary element, for the complete distribution function is determined separately for each fraction, and this is followed by the summation of the curves for all of the fractions. Finally, as will be shown

below, by combining sedimentation and diffusion results in a simple and natural way, we pass from sedimentation constant distribution function $\frac{dc}{ds}$ to the required molecular weight distribution function $\frac{dc}{dM}$.

The study of the molecular weight distribution function of polyamides is of interest not only because it enables us to obtain a deeper understanding of this new and little studied class of macromolecular compounds; it is of still greater importance as a method that enables us to understand and establish with exactness the reaction mechanism by which these substances are formed. The equation for the formation of a polyamide has the following form:



EXPERIMENTAL

Preparation of Samples for Investigation

Four samples of a mixed polyamide were investigated as solutions in methanol. The samples differed in degree of polycondensation. Sample No. 1 had a molecular weight of 30,000 (according to the viscosity of its methanol solution), and the molecular weights of Samples No. 2 and 3 were 20,000 and 46,000 respectively. Sample No. 4 was prepared by heating a mixture of equal amounts of two polyamide fractions, the first fraction having a molecular weight of 15,900, and the second a molecular weight of 58,000 (denoted by 1' and 2' respectively). In order that the mixing might be more complete, the two fractions were first dissolved in methanol and precipitated by pouring the resulting solution into ether. The mixture of fractions was dried in a current of nitrogen and then placed in a sealed tube, which was heated for six hours at 220°. The resulting polyamide had a molecular weight of 31,000 (according to the viscosity of its methanol solution).

Fractionation

Ether was gradually added to 1% solution of the polyamide in methanol until a slight stable turbidity appeared which became gradually more intense as stirring continued. After 2-3 hours, when the amount of precipitate formed had become constant, the fraction was filtered off, washed, and dried in a current of nitrogen under reduced pressure at room temperature. The last fraction was separated after evaporation of the solution to a concentration of 3-4%. In order to avoid losses, after each washing of the precipitate the filtrate was united with the main filtrate containing the residual portion of polyamide. The precipitate sticking to the funnel, walls of the flask, etc. was carefully washed off with hot alcohol; the solution was evaporated down, and the polyamide obtained was assigned to the losses. In Table 1 we give results of the fractionation of the four polymer samples.

TABLE 1

Fractionation of Polyamides

Polyamide Number	Fraction number	Weight of fraction (g)	Weight of losses (g)	Total weight of fraction (g)	Proportion of fraction (by weight)	Viscosimetric mol. wt. of fraction
1	1	0.75	0.20	0.95	0.153	47,500
	2	2.75	0.41	3.16	0.507	29,000
	3	0.75	0.13	0.88	0.141	29,000
	4	0.55	0.11	0.66	0.165	19,500
	5	0.60	0.0	0.60	0.094	6,500
2	1	1.58	0.02	1.60	0.280	26,000
	2	0.79	0.10	0.89	0.155	23,500
	3	0.70	0.12	0.82	0.140	23,500
	4	1.12	0.27	1.39	0.240	14,500
	5	1.05	0.07	1.12	0.185	6,800
3	1	2.86	0.03	2.87	0.162	—
	2	7.80	0.07	7.87	0.444	—
	3	5.38	0.08	5.46	0.310	—
	4	1.42	0.06	1.48	0.084	—
4	1	1.37	0.05	1.42	0.619	—
	2	0.72	0.04	0.76	0.330	—
	3	0.20	0.0	0.12	0.051	—

Experimental Results of Sedimentation Constants and Diffusion Coefficients

The sedimentation constants of the polyamide, dissolved in methanol, were measured in a Svedberg ultracentrifuge [2]. The experiments were carried out at a polyamide concentration of 0.5%. The investigated solution was placed in a Textolite cell fixed in the ultracentrifuge rotor. The measurements were carried out at a rotor speed of 60,000 rpm and at 20-25°. The temperature of the rotor could be measured accurate within 0.1°. For the recording of the sedimentation, Lamm's scale method [3] was used; this utilizes the difference in refractive index between solvent and solution and is based on the proportionality between the refractive index gradient and the concentration gradient. The experiments yield a series of curves, obtained at various times after the beginning of sedimentation, for the variation of the concentration gradient along the cell $\frac{dc}{dx} = f(x)$; from these we find the position of the maximum concentration gradient, i.e., the boundary between the solution and the solvent that has already been freed from dissolved polymer owing to its sedimentation. The $\frac{dc}{dx} = f(x)$ curves have definite widths, owing to the polydispersity of the fraction. The rate at which the maximum of the curve moves corresponds to the sedimentation rate for the "most probable" macromolecules of the given fraction.

From these results, we may calculate the sedimentation constant of the dissolved polymer: for this purpose we use the exact formula for the rate of movement (sedimentation) of a polymer in a centrifugal field:

$\frac{1}{\omega^2 x} v = \frac{1}{\omega^2 x} \frac{dx}{dt} = s$ (s is the sedimentation constant for the distribution maximum, which depends only on the molecular weight of the corresponding macromolecules; ω is the angular velocity of rotation; x is the coordinate, i.e., the distance from the center of the rotor). In this formula a certain degree of inhomogeneity in the centrifugal field is taken into consideration. Integrating this equation, we obtain:

$$\ln x - \ln x_0 = s\omega^2(t - t_0)$$

$[x_0$ is the initial position of the maximum (measured along the radius from the center of the rotor); x is the position at time t].

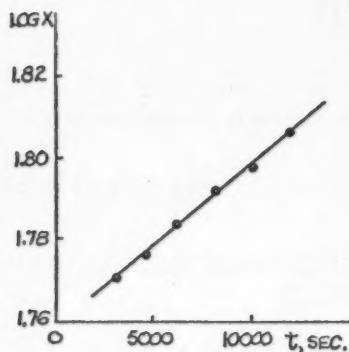


Fig. 1. Graph of $\log x = f(t)$ for a polyamide fraction in methanol at a concentration of 0.5 g per 100 ml.

Hence, if we construct the graph for the change in $\ln x$ for the maximum of the curve against time, a straight line is obtained. Fig. 1 shows such a graph for a typical fraction. The slope of the curve divided by ω^2 gives the constant s for the distribution maximum. The value of s is adjusted to standard conditions (20°) by means of the correction factor

$$k = \frac{\eta_t}{\eta_{20}} \frac{1 - V_{20}\rho_{20}}{1 - V_t\rho_t} \quad (\eta_t \text{ and } \eta_{20} \text{ are the viscosities of the medium at } t^\circ \text{ and } 20^\circ; V_t \text{ and } V_{20}, \rho_t \text{ and } \rho_{20} \text{ are the specific partial volumes of the polymer and the densities of the solution}).$$

Our experimental results are given in Table 2.

One of us has already given a detailed description of the apparatus used for the determination of diffusion coefficients [4]. It consists of a water thermostat in which the cell containing the solution to be investigated is placed, and an optical arrangement for recording the diffusion process by Lamm's method. The solution is formed as a layer under the solvent in a glass cell having a side tube, which, being at the middle of the cell, where the boundary is to be formed, permits the removal of the first portion of the solution, which may mix with the solvent by convection. This method enables the boundary between the layers to be made narrower and sharper.

At definite intervals (six hours) after the establishment of the boundary, the scale is photographed through the solution. The duration of the experiment is 42-48 hours; the temperature of the thermostat is $25 \pm 0.005^\circ$. From the experimental diffusion curves $\frac{dc}{dx} = f(x)$ obtained by examination of the photographs, the curve moments of zero (m_0), first (m_1), and second (m_2) orders are calculated, and hence the diffusion coefficients:

$$D = \left(\frac{m_2}{m_0} - \frac{m_1^2}{m_0^2} \right) \frac{G^2}{2t} \frac{T_{20}\eta_t}{T_t\eta_{20}} = \frac{\sigma^2}{2t}$$

(G is the factor for the photographic magnification of the scale; $\frac{T_{20}\eta_t}{T_t\eta_{20}}$ is the factor necessary for the adjustment of

the diffusion coefficients to normal conditions). From five or six curves relating to one experiment, the calculated values of σ^2 are plotted as a function of t , and the diffusion coefficients are calculated from the slopes of the resulting straight lines. This method of calculation avoids error due to the finite thickness of the boundary between the layers at zero time. The values of diffusion coefficients obtained are given in Table 2.

TABLE 2

Sedimentation Constants and Diffusion Coefficients for Polyamide Fractions

Polyamide number	Fraction number	Sedimentation constant $\cdot 10^{13}$	Diffusion coefficient $\cdot 10^7$	Polyamide number	Fraction number	Sedimentation constant $\cdot 10^{13}$	Diffusion coefficient $\cdot 10^7$
1	1	2.2370	3.8720	3	1 + 2	2.2750	3.3760
	2	2.1138	5.4470		1	2.5060	2.4310
	3	2.0780	5.7620		2	2.2040	3.4660
	4	1.8900	6.0770		3	2.0700	3.6000
	5	1.5450	13.2360		4	1.7340	7.7870
	1 + 2 + 3	2.1440	5.0000	4	1	1.9070	5.0870
2	1	1.9359	4.8620		2	1.7986	6.0777
	2	1.7790	5.9400		3	1.2930	10.8950
	2 + 3	1.8407	5.8200		1''	1.6470	7.5850
	3	1.9200	6.2750		2''	2.4070	3.0160
	4	1.7080	7.1130				
	5	0.9979	23.5000				

In order to calculate the molecular weight it is necessary to know the partial specific volume V of the polyamide in methanol. In order to find this quantity the densities of the pure solvent and of a 0.5% polyamide solution were measured. The calculation of the partial specific volume was made by the formula:

$$V = V_a \left[\frac{1}{m} - \frac{100}{p} \left(\frac{1}{m_0} - \frac{1}{m} \right) \right],$$

[m is the weight of solution in the pycnometer; m_0 is the weight of solvent; $\frac{p}{100} = \frac{gV_a}{m}$ is the proportion of the substance by weight; g is the concentration in g/ml ($g = 0.005$ g/ml); V_a is the volume of the pycnometer (40 ml)]. V_{20} was found to be 0.884.

Table 1 gives the results of determinations of the most probable molecular weights for all of the fractions studied.

Determination of the Distribution Function with respect to Sedimentation Constants for Each Fraction and for the Sample of Polymer as a Whole

The ultracentrifuge gives us, for each fraction, a series of curves $\frac{dc}{dx} = f(x)$ corresponding to various periods of time after the beginning of sedimentation. Examination of the curves $\frac{dc}{dx} = f(x)$ shows that they are somewhat unsymmetrical. For reasons that we shall consider below, in the course of sedimentation the boundary becomes diffuse, i.e., the curve $\frac{dc}{dx} = f(x)$ has a certain width. For this reason the region of the solution corresponding to the beginning of the curve is under a lower centrifugal force than that corresponding to the end of the curve.

Let us examine a point on the curve at Δx from the distribution maximum. The macromolecules corresponding to this coordinate move under a centrifugal acceleration of $\omega^2 x'$, which differs from the acceleration $\omega^2 x$ acting at the distribution maximum. The additional velocity Δv acquired under the action of this extra force will be related to the rate of movement of the peak as follows:

$$\frac{\Delta v}{v} = \frac{\omega^2 x' - \omega^2 x}{\omega^2 x} = \frac{\Delta x}{x}.$$

If we regard the broadening of the curve, i.e., Δx (Δx is the divergence from the central point of the curve), as a quantity that is to a first approximation proportional to the time, we obtain for the displacement due to the

Inhomogeneity of the field:

$$\varphi = \frac{1}{2} \Delta v t = \frac{1}{2} v t \frac{\Delta x}{x} = \frac{1}{2} \Delta x \frac{x - x_0}{x},$$

(x is the coordinate of the center of the curve; $x - x_0$ is the displacement of the peak since the beginning of the experiment). The correction may be up to $\pm 4\%$ of the divergence from the middle point of the curve (Δx). In introducing this correction to the width of the curve, we must, of course, make also corresponding alterations in the ordinates of all points of the curve, so that the area under the curve shall remain unchanged:

$$\frac{dc}{dx} = \left(\frac{dc}{dx} \right) \cdot \left(1 + \frac{x - x_0}{2x} \right).$$

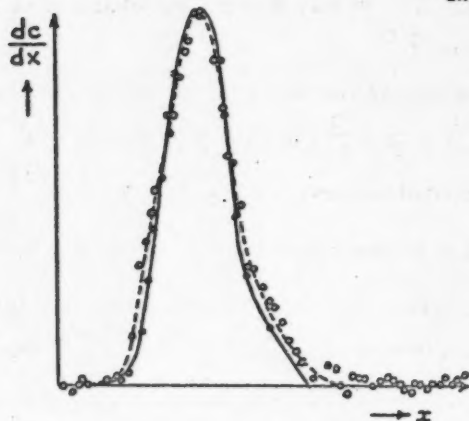


Fig. 2. Experimental sedimentation curve: -o- before correction; -o- after correction for the inhomogeneity of the ultracentrifuge field.

All curves are thus reduced to the form that they would have had if the field of force had been uniform. Fig. 2 shows the experimental curve before and after correction. The correction, although not great, renders the curve symmetrical with respect to the distribution maximum. In such a form the experimental curves can be taken as the basis for the calculations.

Let us examine the physical causes of the broadening of the sedimentation peak with time. They may evidently be of two kinds: first, the polydispersity of the given fraction, and second, diffusion of molecules close to the sedimentation boundary. For polyamides, with their comparatively low molecular weights and corresponding considerable diffusion coefficients, the diffusion broadening will be a quantity of the same order as the broadening due to polydispersity. For this reason a detailed analysis of the phenomenon is required here.

Let us denote the displacement of a macromolecule with respect to the position of the maximum by ξ . Our experimental curve (corrected) can evidently be transformed into a distribution function for macromolecules with respect to displacements simply by transfer of the origin; it will thus be:

$$\frac{dc}{d\xi} = f(\xi).$$

We obtain this function from experiment. The displacement ξ is made up of two statistically independent quantities: ξ_1 , the diffusional displacement of the macromolecules, and ξ_2 , the displacement due to the statistical scatter of molecular sizes within the fraction studied;

$$\xi = \xi_1 + \xi_2.$$

The distribution function with respect to displacements ξ_1 is known from the diffusion laws:

$$\frac{dc}{d\xi_1} = \varphi_1(\xi_1) = \frac{c_0}{\sqrt{4\pi Dt}} e^{-\frac{\xi_1^2}{4Dt}}.$$

There is also, of course, a certain scatter of the diffusion constant D within each fraction, but this gives only a correction of the second order in the distribution function. The distribution function with respect to the displacements ξ_2 , i.e., $\frac{dc}{d\xi} = \varphi_2(\xi_2)$, is the required distribution function for the polydisperse substance with respect to sedimentation constants. Since the displacements ξ_1 and ξ_2 are statistically independent, in accordance with statistical laws we obtain:

$$\frac{dc}{d\xi} = f(\xi) = \int_{-\infty}^{\infty} \varphi_1(x) \varphi_2(\xi - x) dx = \int_{-\infty}^{\infty} \text{Be}^{-\frac{x^2}{4Dt}} \varphi_2(\xi - x) dx.$$

Hence, the function sought, $\varphi_2(\xi)$, is found as the solution of an integral equation of the Feldholm type, the left hand side of which is the function $f(\xi)$, which we know in graphical form (the experimental curve). This equation may be solved by various methods, according to the form of the function f , but it is particularly simple to solve when the empirical function $f(\xi)$ can be closely approximated by a Gauss function, which is indeed so in our case. A Gauss curve is shown in Fig. 3, and the empirical points for the fraction that we used to demonstrate the method of calculation are indicated on this curve. It will be quite obvious that the experimental results fit the Gauss curve very well. The same applies to a large number of experimental curves that we have obtained. As will be shown later, this fact is a consequence of the fact that within every fraction the molecular weight distribution function is Gaussian.

If we write $f(\xi) = Ae^{-\alpha^2 \xi^2}$, and also $\varphi_1(\xi) = Be^{-\beta^2 \xi^2} = Be^{-\frac{\xi^2}{4Dt}}$, we may show that the solution of the integral equation is also a Gauss function, i.e., the required $\varphi_2(\xi_2) = ce^{-\gamma^2 \xi_2^2}$.

Simple algebraic manipulation enables us to prove this theorem and also to find the relation between the constants characterizing the distribution range. It is found that $\frac{1}{\alpha^2} = \frac{1}{\beta^2} + \frac{1}{\gamma^2}$, in which α^2 is an empirical quantity that may be found from the value of ξ at half of the height of the curve, when we have $\frac{1}{2} = e^{-\alpha^2 \xi_{1/2}^2}$, and $\alpha^2 = \frac{\ln 2}{\xi_{1/2}^2}$, β^2 is $\frac{1}{4Dt}$; and γ^2 characterizes the required range of the distribution function. We require, however, the distribution function with respect to sedimentation constants, and not with respect to displacements ξ_2 . Let us suppose that the required distribution function with respect to sedimentation constants is $\frac{dc}{ds} = Ke^{-\delta^2(s-s_0)} = Ke^{-\delta^2 \Delta s^2}$, in equation $\xi_2 = (s-s_0)\omega^2 \underline{x}t$, we find that $\gamma^2 = \frac{\delta^2}{(\omega^2 \underline{x})^2 t^2}$, and finally that $\frac{1}{\alpha^2} = 4Dt + \frac{(\omega^2 \underline{x})^2}{\delta^2} t^2$, in which δ^2 is the required quantity.

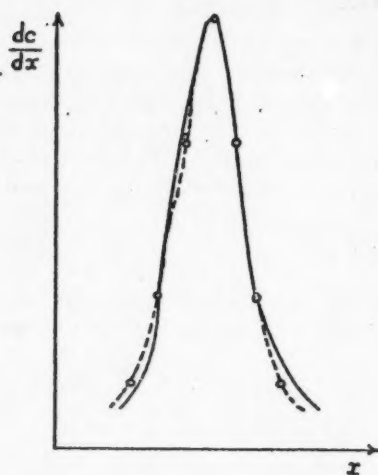


Fig. 3. ——— = experimental sedimentation curve; ----- = corresponding Gaussian curve.

We may now turn to the treatment of the experimental curves corresponding to sedimentation times t_1, t_2, t_3 , etc.. We must point out that for the calculation of the breadth of the fraction very short times, i.e., near to the beginning of the experiment, must not be taken, since the start of sedimentation is not very definite in the ultracentrifuge. During the acceleration of the rotor, mixing occurs, but at a certain time sedimentation begins. This time does not generally coincide with that at which the ultracentrifuge has worked up to full speed. Also, in the initial period, when the sedimentation boundary has not yet separated from the meniscus, diffusion occurs only in one direction, i.e., with reflection from the boundary of the liquid. The diffusional broadening will, therefore, be approximately one-half as great as that calculated for free diffusion. We can leave these complications out of account if we take times that are not too near to the start of the experiment. For two times t_1 and t_2 we may then write the difference equation:

$$\frac{1}{\alpha_2^2} - \frac{1}{\alpha_1^2} = 4D(t_2 - t_1) + \frac{(\omega^2 \underline{x})^2}{\delta^2} (t_2^2 - t_1^2).$$

From this the required distribution parameter δ^2 can be found.

The calculation is generally carried out for several experimental curves. The scatter of the values of δ^2 found is not great, and the mean value of δ^2 , characterizing each fraction, is found. It must be pointed

out that in these considerations no arbitrary elements have been admitted. The fundamental integral equation was deduced from the principles of statistics, and it can be solved for the most varied experimental relationships

$\frac{dc}{d\xi} = f(\xi)$. The fact that our results are closely approximated by means of a Gauss function enables the calculations to be considerably simplified, but is in no way essential to the performance of our scheme of calculation. Table 3 gives the values found for the sedimentation constants \underline{s}_0 , the widths of the distribution curves with respect to sedimentation constants for all of the fractions obtained, and also δ^2 , the quantity characterizing the distribution curve $\frac{dc}{ds} = Ke^{-\delta^2(s-s_0)^2}$.

TABLE 3

Experimental Results Relating to Sedimentation Constant Distribution Functions of Polyamides

Polyamide number	Fraction number	Proportion of fraction by weight	Sedimentation constant $\cdot 10^{13}$	Width $\cdot 10^{13}$ of the sedimentation constant distribution curve	Quantity δ^2 characterizing the distribution curve $\cdot 10^{-25}$
1	1 + 2 + 3	0.801	2.1110	1.0000	69.00
	4	0.105	1.8900	0.2640	9.90
	5	0.094	1.5450	0.4670	3.14
2	1	0.280	1.9359	0.2270	13.39
	2 + 3	0.295	1.8407	0.0802	108.00
	4	0.240	1.7080	0.2240	13.75
	5	0.185	0.9979	0.3800	4.67
3	1 + 2	0.598	2.2750	0.0930	79.80
	3	0.317	2.0700	0.3000	7.67
	4	0.085	1.8090	0.3424	5.90
4	1	0.620	1.9070	0.3610	6.70
	2	0.330	1.7986	0.1120	55.30
	3	0.050	1.2930	0.2630	9.96
	2''	0.500	2.3155	0.0704	139.00
	1''	0.500	1.6470	0.3910	4.51

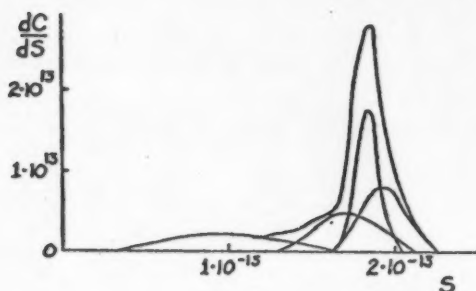


Fig. 4. Sedimentation constant distribution curve for Polyamide Sample No. 1.

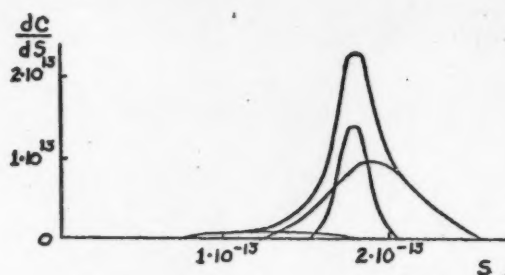


Fig. 5. Sedimentation constant distribution curve for Polyamide Sample No. 2.

In Figures 4 and 5 sedimentation constant distribution curves are constructed from the data so provided.

It must be pointed out here that the fractions obtained by precipitation do not at all fulfill the fundamental requirement of the extensively used method for the construction of differential and summative distribution curves, namely, that the lowest molecular weight for a given fraction must be higher than the highest molecular weight of the preceding fraction. It must, therefore, be concluded that the method of constructing summative and differential distribution curves from fractional precipitation data cannot be regarded as rigorously correct.

SUMMARY

1. A method has been developed for the study of the sedimentation constant distribution function of polymers. It consists in separation of the polymer into a number of fractions by precipitation from solution, followed by the study of each fraction separately by means of ultracentrifuge and diffusion experiments.
2. It has been shown, a number of polyamides being taken as examples, how it is possible to obtain the sedimentation constant distribution function for each fraction by subtraction of the broadening of the sedimentation diagram due to diffusion from the total broadening of the boundary of the sedimenting fraction in the ultracentrifuge.
3. Owing to the fact that the experimental curves for the separate fractions, after correction for the effect of the inhomogeneity of the centrifugal field, are closely approximated by a Gauss function, all of the calculations become extremely simple.

4. By summation of the distribution functions obtained for separate fractions, taking into account the relative weights of the fractions, we may obtain the distribution functions for the whole polymer samples. By this method we have obtained the summative distribution functions for four polyamide samples varying in degree of polycondensation.

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INVESTIGATION BY THE ULTRACENTRIFUGE SEDIMENTATION METHOD OF THE MOLECULAR WEIGHT DISTRIBUTION FUNCTION OF POLYAMIDES

COMMUNICATION 2: MOLECULAR WEIGHT DISTRIBUTION OF POLYAMIDES, AND THE MECHANISM OF POLYCONDENSATION*

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Conversion to Molecular Weight Distribution Functions

If the sedimentation constant and diffusion coefficient are known, it is not difficult to determine also the molecular weight of the polymer, since

$$s = \frac{M(1-v\rho)}{f},$$

in which M is the molecular weight; v is the partial specific volume of the polymer; ρ is the specific weight of the solvent; and f is the coefficient of friction, given, according to Einstein's law, by $f = \frac{RT}{D}$, so that $M = \frac{RTs}{D(1-v\rho)}$ (R is the gas constant). We know the sedimentation constant for the distribution maximum of every function, and we know the weight average value of the diffusion coefficient, i.e., $\bar{D} = \frac{\int Ddc}{\int dc}$, since it is this average value that is found from the experimental diffusion curves by calculation based on the method of moments.

It is easy to show that in our case, in which the sedimentation constant distribution function for each fraction is a symmetrical Gauss function, the average value of the diffusion coefficient is identical with the diffusion coefficient at the distribution maximum of the fraction. The distribution with respect to sedimentation constants is given by:

$$\frac{dc}{ds} = Ke^{-\delta^2(s-s_0)^2} \text{ (Gauss function),}$$

(s_0 is the most probable sedimentation constant within the given fraction). We may pass from this function to the distribution function with respect to diffusion coefficients if we take into account the fact that the diffusion coefficient is a single-valued function of the sedimentation constant: $D = f(s)$. Since the sedimentation constants within the fraction are close to s_0 , then expressing the function f as a series for such values of s and confining ourselves to the first term, we obtain:

$$D - D_0 = \kappa(s - s_0), \text{ in which } \kappa = \left(\frac{df}{ds}\right)_{s=s_0}.$$

Hence, for the distribution function with respect to diffusion coefficients the Gauss function is again valid to the first approximation:

$$\frac{dc}{dD} = K'e^{-\epsilon^2(D-D_0)^2}.$$

In a similar way it can be shown that the molecular weight distribution function is also expressed by a Gauss function. It follows that $D = D_0$, i.e., for every fraction the average diffusion coefficient is the most probable. The diffusion coefficients that we have measured for different fractions may, therefore, be assigned with sufficient accuracy to the "most probable" macromolecules within the fractions, and for these the sedimentation constants have already been determined. From these results, therefore, we may make fully rigorous calculations of molecular weights.

On the basis of these considerations, using the determined values of sedimentation constants and diffusion coefficients, we have calculated the values of the molecular weights of the polyamide fractions investigated (Table 1).

* This paper reports the continuation of work described in Communication 1.

From these data the functional relationships $s = \varphi(M)$ and $D = \varphi'(M)$ can be constructed. It is, however, more rational to present these relationships in an analytical form by the use of the equations of Debye and Kirkwood [1]: $s = KM^n$ and $D = K'M^{1-n}$. According to Debye's equation, the index n depends on the hydrodynamic properties of the macromolecule in solution. If the solvent flows freely past the macromolecule, i.e., if it has a curved thread-like form, $n = 0$, i.e., the sedimentation will cease to depend on the molecular weight. If, on the contrary, the macromolecule is globular and the liquid flows round it, but cannot penetrate it, $n = 0.5$.

TABLE 1

Molecular Weights of Polyamides Determined with the aid of the Ultracentrifuge

Polyamide number	Fraction number	Sedimentation constant $\cdot 10^{13}$	Diffusion constant $\cdot 10^7$	Molecular weight
1	1	2.2370	3.8720	40,060
	2	2.1137	5.4470	28,450
	3	2.8780	5.7620	22,440
	4	1.8900	6.0720	22,800
	5	1.5450	13.2360	8,550
	1 + 2 + 3	2.1440	5.0000	31,440
2	1	1.9359	4.8620	29,190
	2	1.7790	5.9400	21,960
	2 + 3	1.8407	5.8200	23,200
	3	1.9200	6.2750	22,430
	4	1.7080	7.1130	17,600
	5	0.9979	23.5000	3,110
3	1	2.5060	2.4310	75,600
	1 + 2	2.2750	3.3760	49,400
	2	2.2040	3.4660	46,600
	3	2.0700	3.6000	42,160
	4	1.7340	7.7870	16,330
4	1	1.9070	5.0870	27,500
	2	1.7986	6.0777	21,700
	3	1.2930	10.8950	8,700
	1''	1.6470	7.5850	15,900
	2''	2.4070	3.0160	58,510

It can be readily shown that our experimental results are closely described by the equation of Debye and Kirkwood. For this purpose it is necessary to plot $\log s$ against $\log M$, but it is more convenient to do this for $\log D$ and $\log M$, since the difference between the diffusion coefficients for different fractions is greater than that between the sedimentation constants. It is then necessary to pass by calculation from $D = K'M^{1-n}$ to $s = KM^n$, which is readily done with the aid of the known relationship between these three quantities. It will be seen from Figs. 1, 2, and 3 that the dependence of $\log D$ on $\log M$ is expressed by straight lines. The power index varies somewhat for different samples, but always remains within the limits 0.30-0.33, i.e., the macromolecules of polyamides tend toward a globular form that is not readily penetrated by the solvent. The explanation of this behavior may be that the polyamide chain has a considerable amount of flexibility, owing to the considerable dilution of the peptide linkages by methylene groups.

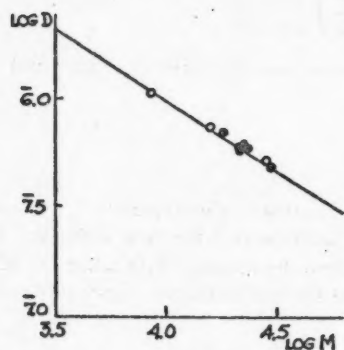


Fig. 1. Dependence of $\log D$ on $\log M$: o = for Polyamide No. 4; • = for Polyamide No. 1.

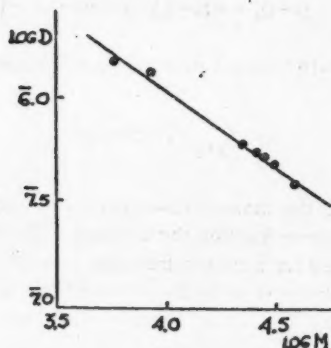


Fig. 2. Dependence of $\log D$ on $\log M$ for Polyamide No. 2.

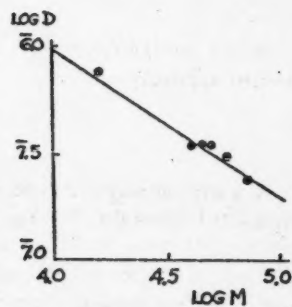


Fig. 3. Dependence of $\log D$ on $\log M$ for Polyamide No. 3.

We may now readily transform the distribution functions $\frac{dc}{ds} = f(s)$ found above into the required molecular weight distribution functions $\frac{dc}{dM} = \varphi(M)$; for $\frac{dc}{dM} = \frac{dc}{ds} \cdot \frac{ds}{dM} = \frac{dc}{ds} \cdot K \cdot n \cdot M^{n-1}$. We shall apply this formula to our experimental results. The relationships found, $D = K' M^{1-n}$ and $s = KM^n$ are given in Table 2.

TABLE 2

Relationships between the Diffusion Coefficient D , the Sedimentation Constant s , and the Molecular Weight for Polyamides

Polyamide number	D	s	ds/dM
1 + 4	$7.08 \cdot 10^{-4} \cdot M^{-0.7}$	$9.657 \cdot 10^{-15} \cdot M^{0.3}$	$2.897 \cdot 10^{-15} \cdot M^{-0.7}$
2	$4.842 \cdot 10^{-4} \cdot M^{-0.67}$	$6.604 \cdot 10^{-15} \cdot M^{0.33}$	$2.179 \cdot 10^{-15} \cdot M^{-0.67}$
3	$5.129 \cdot 10^{-4} \cdot M^{-0.68}$	$6.996 \cdot 10^{-15} \cdot M^{0.32}$	$2.239 \cdot 10^{-15} \cdot M^{-0.68}$

The final molecular weight distribution functions for all of the samples that we have studied are given in Figs. 4, 5, and 6.

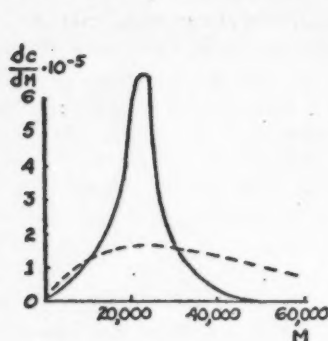


Fig. 4. Experimental molecular weight distribution curve for Polyamide No. 1

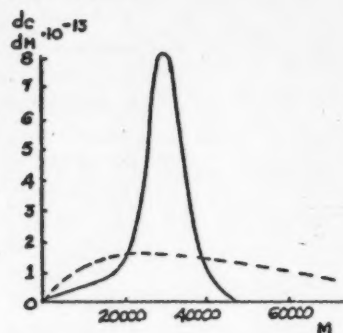


Fig. 5. Experimental molecular weight distribution curve for Polyamide No. 2.

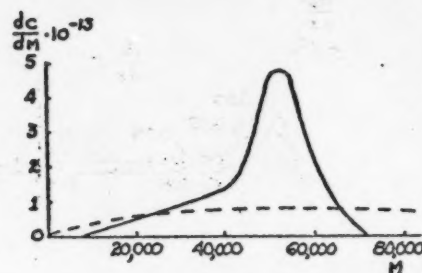


Fig. 6. Experimental molecular weight distribution curve for Polyamide No. 3.

In order to determine the concentrational dependence of the sedimentation constants and diffusion coefficients, special experiments were undertaken. It was found that for all of the polymers studied the concentrational dependence was insignificant, and could not have any appreciable effect on the results of the investigation. For this reason, we carried out all measurements at a standard polymer concentration (0.5%).

Mechanism of Linear Polycondensation, and the Theoretical Molecular Weight Distribution Function

On the basis of our results it is possible to obtain a correct picture of the mechanism of the linear-polymerization reaction. At the present time two views exist on the mechanism of this reaction. One of these, which is widely held in American work, was advanced by Flory [2], and the second was advanced by one of us [3].

Flory regards the process of linear polycondensation as a stepwise reaction of bifunctional molecules, and considers the addition of a monomer molecule to any free functional group (in the case of a polyamide, a carboxyl or amino group) to have the same probability whether the latter belongs to another monomer molecule or is the end group of a polymer chain. Also, Flory regards the already formed polymeric macromolecules as being very stable, being able only to undergo growth as the reaction progresses. The molecular weight distribution function derived by Flory on the basis of these assumptions has the following form:

$$\frac{dc}{dx} = W_x = x(1-p)^2 p^{x-1}$$

(W_x is the fraction by weight of the molecules having a degree of polymerization of x ; p is the extent to which the functional groups enter into reaction (progress of reaction). It will be clear that in such a case the number of

molecules of all possible sizes contained in the reaction product can be expressed for any given moment as $N = N_0(1-p)$ (N_0 is the number of monomer molecules). The number of molecules having a degree of polymerization of x will be:

$$N_x = N_0(1-p)p^{x-1}$$

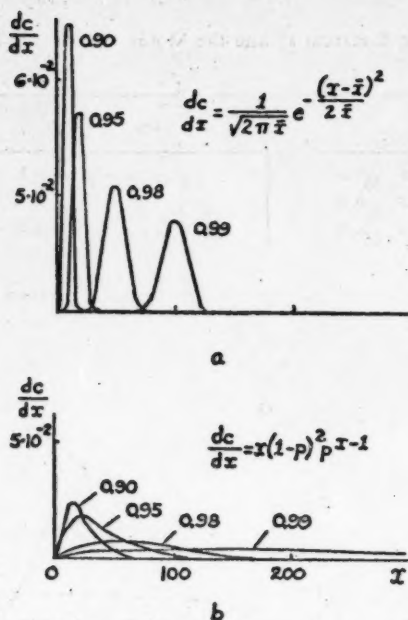


Fig. 7. Molecular weight distribution curves for various values of the progress of reaction: (a) — calculated on the basis of the proposed theory; (b) — calculated from Flory's theory

more bonds it contains that are capable of being broken, and the greater, therefore, is the tendency for such a molecule to undergo degradation. Hence, it is mainly the longest molecules that are degraded.

Owing to the occurrence of these numerous exchange reactions, there is a constant reshuffling of the repeating units in the polymer molecules, and finally a statistical equilibrium molecular weight distribution is established which corresponds to the greatest probability, or entropy. It will be clear that under such circumstances, the molecular weight distribution function will be quite different from that required by Flory's theory. A number of results of this character have already been obtained in studies of the polydispersity of polyamides and polyesters by fractional precipitation from solution [7, 8]. The most reliable results, however, are obtained by means of the ultracentrifuge, which is the ideal apparatus for the study of the polydispersity of macromolecular compounds.

In Figures 4, 5, and 6, we give the distribution curves for the three polyamides No. 1, 2, and 3, as found experimentally by us, and for comparison we show by the broken lines the distribution curves for the same values of the progress of reaction, as calculated from Flory's theory. As will be seen, there is a very great difference between the distribution to be expected on Flory's theory and that actually observed, and this fact must be regarded as a decisive argument against this theory.

Our results again show in very convincing fashion the presence of degradation reactions and their important role in the polycondensation process. This may be illustrated by reference to Polyamide No. 4, which was obtained by heating a mixture of two fractions having molecular weights of 15,000 and 58,000 respectively. Fig. 8 shows the molecular weight distributions for these fractions before heating, and the distribution for the polyamide formed when a mixture of these fractions is heated. The great change produced in the distribution as

The characteristic feature of the theory proposed by Flory is the constantly increasing width of the curve expressing the molecular weight distribution function as the extent of polymerization increases, as can be seen from Fig. 7(b). This implies that the polydispersity of polymers will increase enormously with rise in molecular weight.

The other point of view on the mechanism of the linear-polycondensation reaction was advanced by one of us [3], and has been substantiated by numerous investigations. It differs from the first point of view in two fundamental respects: first, it recognizes the major role of exchange, mainly destructive, reactions between polymer and monomer molecules, and also between polymer molecules of different degrees of polymerization; and second, it takes into account the fact that the probability of the destruction of macromolecules is directly proportional to their size, i.e., molecular weight. The tendency of macromolecules to undergo degradation was established in studies of a large number of examples of acidolysis and aminolysis reactions for polyamides [4, 5], acidolysis and alcoholysis reactions for polyesters, and also exchange reactions for polyesters [6] (studied in investigations on polyamidoesters) and various other reactions. In the majority of cases these exchange reactions are destructive and lead to breakdown of already formed macromolecules to shorter ones; and the bigger the molecule, the

a result of the interaction of the fractions will be clearly seen. It is important also to note the close resemblance between the distribution for this polymer, which was not prepared in the usual way, and the distributions for the other three polyamides, which were prepared as usual from the corresponding low-molecular-weight starting materials. It is quite clear that this phenomenon arises solely as the result of degradative exchange reactions.

In order to determine what is to be expected on the basis of the more correct point of view on the mechanism of polycondensation processes, we shall derive a new formula for the distribution function for the case of complete statistical equilibrium in the polycondensation reaction. Since we can always imagine a sequence of secondary reactions (for a given progress of reaction p) such that any monomeric unit will be transferred from an arbitrary position in one polymer chain to an arbitrary position in another, the problem is equivalent to the classical problem of probability theory concerning the distribution of N_0 balls (chain units) into N boxes (macromolecules), all of the events (i.e., the entry of a ball into one or other box) being mutually independent. As is well known, if we denote the number of boxes in which there are x balls by N_x (the number of x -meric macromolecules), we obtain:

$$W_x = N_x x = \frac{x \left(\frac{N_0}{N} \right)^x}{x!} e^{-\frac{N_0}{N}} \approx \frac{1}{\sqrt{2\pi x}} e^{-\frac{(x-\bar{x})^2}{2\bar{x}}}$$

(x is the degree of polymerization; W_x is the fraction of x -mers by weight; \bar{x} is the average degree of polymerization of the polymer obtained, and is given

by $\bar{x} = \frac{N_0}{N} = \frac{1}{1-p}$). The distribution function, therefore, is expressed by a Gaussian curve, the half-width of which, measured at the middle point of its height, will be given by:

$$\Delta x = (x - \bar{x})_0 = \sqrt{2 \ln 2 \cdot \bar{x}} \approx \sqrt{1.4 \bar{x}}$$

Such curves, calculated for various values of p from 0.9 to 0.99 are given in Fig. 7(a). It will be seen that they are indeed quite different from the Flory curves. As the extent of polycondensation increases, the breadth of the distribution increases comparatively little, proportional, in fact, to $\sqrt{\frac{1}{1-p}}$.

In Table 3 we give the experimentally found proportionality coefficients, calculated as

$$K = \frac{\Delta M_{\text{exp}}}{\sqrt{\bar{x}} \cdot 113} = \frac{\Delta x_{\text{exp}}}{\sqrt{\frac{1}{1-p}}}$$

(ΔM_{exp} is the half-width of the experimental molecular weight distribution curve measured at half-height; 113 is the weight of the repeating unit).

The proportionality coefficient K can be regarded as practically constant for all of the three values of the progress of reaction. Hence, as the theory of the statistical equilibrium distribution predicts, the breadth of the curve increases proportionally to the root of the average degree of polymerization of the sample. At the same time, the absolute value of the coefficient K is about 2.5 times as great as that calculated from the theory. This indicates that a definite correlation exists between the closest units of the polyamide chain, i.e., that any particular unit cannot occupy, independently of others, any position in any macromolecule. One of the sources of such correlation is clear.

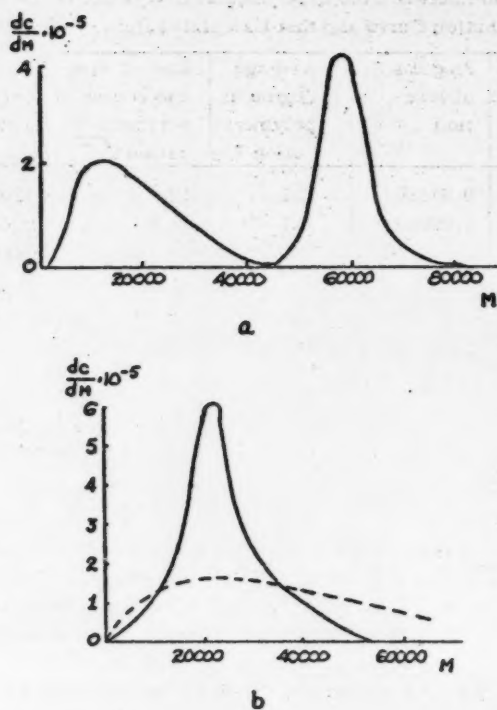


Fig. 8. Molecular weight distribution curves: (a) - for two fractions of mixed polyamide; (b) - for the same, after being mixed and heated together.

TABLE 3

Relation between the Experimental Half-width of the Molecular Weight Distribution Curve and that Calculated from the Proposed Formula

Poly-amide No.	Progress of reaction	Average degree of polymerization \bar{x}	Root of average degree of polymerization $\sqrt{\bar{x}}$	Half-width of exptl. mol. wt. distribution curve	Proportionality coefficient K
2	0.99380	161	12.6	4200	2.95
1	0.99540	217	14.8	5000	2.99
4	0.99690	322	18.0	6400	3.14

The essential point is that immediately after a diamine unit a dicarboxylic acid unit is bound to occur, so that the correlation between the two adjacent units is obvious. Let us suppose that the correlation extends over ν consecutive units. Mathematically this means that the size of the elementary unit has grown by a factor of ν , and the total number has been correspondingly reduced by a factor of ν . Hence:

$$K = \frac{\Delta M_{\text{exp}}}{\sqrt{-\frac{\bar{x}}{\nu}} \cdot 113\nu} = \frac{\Delta M_{\text{exp}}}{\sqrt{\bar{x}\nu} \cdot 113}$$

In order that the experimental results shall satisfy the theoretical relationship, according to which $K = \sqrt{2 \ln 2} \approx 1.2$, we must make $\sqrt{\nu} = 2.5$, i.e., $\nu \approx 6$. The fact that the value of ν is greater than two and is identical for all of the polymers that we have studied indicates that in a mixed polymer there is a certain regularity in the order in which the various monomer units occur.

Let us examine also the so-called coefficient of polydispersity $\frac{M_w}{M_c}$ (M_w is the weight average molecular weight, and M_c is the number average molecular weight). With increase in the progress of reaction, experiment shows that $\frac{M_w}{M_c}$ falls and tends to unity. The same conclusion follows from our theory for the equilibrium distribution. According to Flory, on the other hand, the coefficient of polydispersity should rise as the average molecular weight of the product increases, and it should tend to the value of two.

The results of this investigation, therefore, are in direct conflict with the theory that regards polycondensation as simple stepwise chain growth. It follows from our results that the polycondensation process proceeds as a complex system of destructive and synthetic reactions, in the course of which the growing polymer molecules continually interact among themselves and with the molecules of the starting materials. As a result, the molecular weight distribution attained is close to an equilibrium one.

SUMMARY

1. Sedimentation constants and diffusion coefficients have been determined in the ultracentrifuge for four samples of polyamides.
2. On the basis of these examples a fairly rigorous method has been developed for the determination of the molecular weight distribution function for polymers.
3. The experimentally obtained distribution functions have been compared with the theoretical curves required by Flory's theory, and the invalidity of this theory has been demonstrated.
4. The results obtained are explained as a consequence of the occurrence, during the polycondensation process, of exchange and degradation reactions between the polymer molecules themselves and between polymer and monomer molecules; as a result of these reactions, the distribution function obtained is fairly narrow.
5. It is pointed out that the widely used methods, based on precipitation from solution, for the fractionation of polymers and the determination of their molecular weight distribution are unsatisfactory.
6. It is concluded that, in solution, polyamides behave as if they consist of compact, not readily penetrated, globular particles; which is an indication of the considerable flexibility of their chains.

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SOME REACTIONS OCCURRING DURING THE POLYMERIZATION OF BUTYL VINYL ETHER

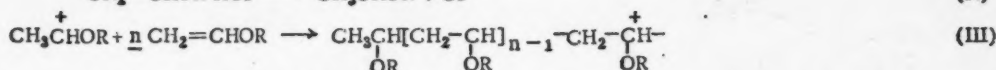
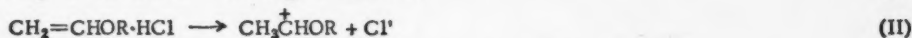
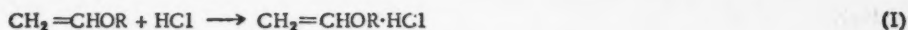
M. F. Shostakovskiy and V. A. Gladyshevskaya

The study of the polymerization processes of alkyl vinyl ethers is of considerable interest owing to the fact that these compounds comprise a large group of polymerizable substances of particularly high reactivity. The high chemical activity of these compounds is dependent on the presence of a double bond in immediate proximity to the ether oxygen [1]. Owing to this structural peculiarity, the properties of the double bond of a vinyl ether are greatly different from those of the double bonds of many compounds that may be included under the general heading of ethylene derivatives. The high reactivity of alkyl vinyl ethers comes into particular prominence in studies of ionic polymerization and copolymerization processes [2].

Vinyl ethers form one of the classes of compounds that can react both by the ionic and by the free-radical mechanism [3]. According to the nature of the catalysts used in the polymerization of alkyl vinyl ethers, the mechanism of the process that occurs will be ionic or free-radical in type. A number of catalysts, such as mineral acids, metal chlorides, and halogens [4, 5, 6, 7], induce the polymerization of vinyl ethers by an ionic process [3]. The course of the process is determined by the properties of the catalyst and the temperature.

As our previous investigations have shown, polymerization processes occurring under the catalytic action of FeCl_3 and HCl proceed most smoothly at a temperature close to the boiling point of the vinyl ether [8].

In this connection it may be assumed that at the boiling point of the vinyl ether, decomposition of the intermediate complex (I) occurs with formation of an active molecule of the vinyl ether (II), which initiates a propagating polymer chain (III) [9]:



Termination of the ionic polymer chain may occur in various ways. There are indications in the literature [10] that the termination of polymer chains may occur by the action of traces of impurities, such as alcohols.

We have already pointed out the importance of the purity of alkyl vinyl ethers in polymerization processes [11]. The main impurities found in alkyl vinyl ethers are the alcohols employed as starting materials in the preparation of the ethers. Alcohols present in the original vinyl ethers take part in chain-termination reactions, leading to the formation of low-molecular-weight compounds. Also, alcohols readily react with the original alkyl vinyl ethers, forming acetals [12]. A study, however, of the composition and structure of the resulting acetals is not sufficient for the elucidation of the part played by alcohols in the polymerization process. We have therefore undertaken the present investigation in order to elucidate further the action of alcohols, which have been introduced into the reaction mixture at various times during the polymerization.

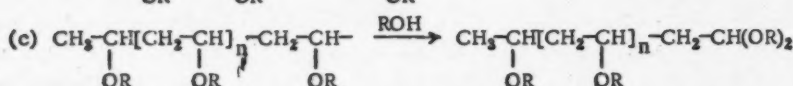
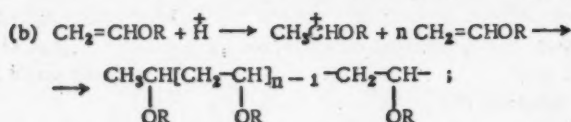
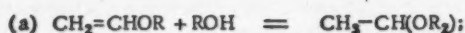
In the present investigation we have studied the reactions of mixtures of butyl vinyl ether and butyl alcohol. First of all we studied a mixture of 92% of butyl vinyl ether and 8% of butyl alcohol, which is an azeotropic mixture [13]. In the investigation of the chemical reactions of such mixtures, the question of the possibility of obtaining reproducible results is of great interest. For this purpose a series of experiments was carried out in which standard conditions were observed, and the products were characterized by determinations of viscosity (1 g of the substance in 100 ml of benzene), refractive index, and molecular weight. As a result of this work, it was found possible to obtain products that were very closely alike with respect to their constants in all of the experiments (Table 1).

As a result of further treatment of the products, it was shown that reaction proceeded in several directions in the mixture, the final result being the formation of acetaldehyde dialkyl acetal, polymer, and possibly other

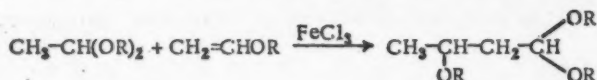
substances. It was found possible to fractionate the polymer formed from the azeotropic mixture into two fractions differing considerably from each other in degree of polymerization (Table 2). However, the molecular weight even of the first fraction, which had the higher degree of polymerization, was considerably less than that of the product of the polymerization of purified butyl vinyl ether [14]. This indicates that in the polymerization of the azeotropic mixture the butyl alcohol present brings about the termination of the polymerization process.

The part played by butyl alcohol in the formation of acetals and the termination of the polymerization process is seen particularly clearly in the experiments in which the butyl alcohol was introduced into the reaction mixture at various times during the polymerization. To an extent depending on the stage of the polymerization process, which was established by refractive index measurements, addition of butyl alcohol greatly impeded the formation of macromolecular products (Table 4).

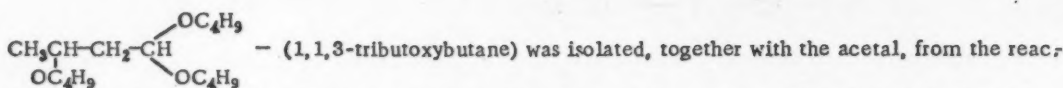
The courses of all of the above described reactions can be represented by the following schemes:



It was found, however, that the polymerization processes of alkyl vinyl ethers containing additions of various alcohols are even more complicated than those represented in the above schemes. In these no account is taken of the fact that an extremely active new substance, the acetal of the corresponding alcohol, is formed. This compound, we consider, has a mobile hydrogen, and as a result, reaction in the following direction may readily occur:

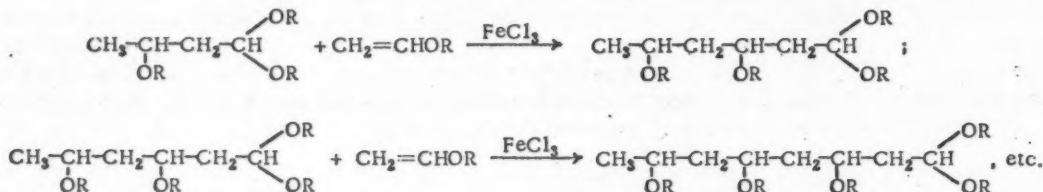


(R is alkyl).

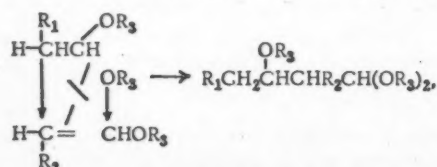


tion products of a mixture of two molecular proportions of butyl vinyl ether and one of butyl alcohol. In this process a polymer of very low molecular weight (564) was also formed.

The formation of 1,1,3-tributoxybutane by the reaction of the acetal with the alkyl vinyl ether is very interesting, since, as a further development of the idea of reaction between 1,1,3-tributoxybutane, we may postulate gradual growth of the chain, proceeding as follows:



i.e., the chain grows as a result of step-by-step polymerization. This does not exclude, however, the possibility of a second mechanism of chain growth, represented in a paper by Hoaglin and Hirsh [15] as follows:



(R₁ and R₂ are hydrogen atoms or alkyl radicals; R₃ is an alkyl radical).

It may be assumed also that the low-molecular-weight polymer isolated in the described transformations may be formed in the following two ways: 1) ionic chain polymerization; 2) stepwise polymerization. In its molecular weight it corresponds to 1,1,3,5,7-pentabutoxyoctane.

These suppositions, and also the experimental proof of the true mechanism of the reactions described, will form the object of our further investigations.

The formation of 1,1,3-trialkoxybutanes is described in the paper of Hoaglin and Hirsh [15], but they do not characterize 1,1,3-tributoxybutane, which we isolated from the reaction products of the mixture of two molecular proportions of butyl vinyl ether and one molecular proportion of butyl alcohol; in the present investigation we have therefore carried out a special synthesis of 1,1,3-tributoxybutane.

It has therefore been established that, when alkyl vinyl ethers contain alcohols, the latter play an important part in many ways in the course of the polymerization process. The presence of an alcohol in the reaction mixture may lead to the occurrence of various chemical reactions that will greatly affect the composition and properties of the products.

EXPERIMENTAL

1. Starting Materials. With a view to their purification, the starting materials were treated as follows:

a) Butyl alcohol was washed with dilute sulfuric acid and with sodium bisulfite solution, and was boiled for 90 minutes with a 20% solution of caustic soda. It was then washed with water, dried over potassium carbonate and then over barium oxide, and then distilled from a flask fitted with a Vigreux column [16]. After purification in this way, the butyl alcohol had the following constants: b.p. 117.6° (760 mm); n_D^{20} 1.3995; d_4^{20} 0.8100; η 2.816 centipoise.

b) Butyl vinyl ether (commercial product) was purified by washing five times with equal volumes of water, drying, and treating with sodium. The ether was then distilled, and for the experiments the fraction of b.p. 93.5° was taken; it had the following constants: n_D^{20} 1.4020; d_4^{20} 0.7795; η 0.439 centipoise.

From these components two mixtures were made: 1) the azeotropic mixture (92% of butyl vinyl ether and 8% of butyl alcohol); and 2) a mixture of two molecular proportions of butyl vinyl ether and one of butyl alcohol.

c) The catalyst used was a 5% solution of ferric chloride in absolute butyl alcohol.

2. Study of the Reactions of the Azeotropic Mixture of Butyl Vinyl Ether and Butyl Alcohol. The reaction was carried out in a three-necked round-bottomed flask fitted with mercury-sealed mechanical stirrer and reflux condenser. The azeotropic mixture (100 g) was poured into the flask and heated to 95-97°. At this temperature catalyst was added in small portions (0.04 g) at a time. As each portion of catalyst was added, the temperature of the reaction mixture rose. Addition of catalyst was discontinued when its addition caused no temperature rise, thus indicating that reaction was complete. In the course of the experiment, altogether 0.24 g of catalyst was added. The experiment lasted for two hours. Further experiments (Table 1, Expt. No. 4) showed that reduction of the total amount of catalyst to 0.06 g had no effect on the final result of the process so long as it was all added at once and the duration of the reaction was increased to four hours.

By observance of the above-described conditions, it was found possible to obtain products that were closely alike with respect to their constants in all of the experiments (Table 1).

TABLE 1

Constants of Products Obtained by Reaction of an Azeotropic Mixture of Butyl Vinyl Ether and Butyl Alcohol

Expt. No.	n_D^{20}	d_4^{20}	Viscosity of soln. of 1 g polymer in 100 ml benzene (centipoise)	Yield (%)
1	1.4455	0.9043	0.676	95
2	1.4460	0.9048	0.676	94
3	1.4455	0.9038	0.676	96
4	1.4460	0.9045	0.676	95

The viscosity of a solution of 1 g of the polymer in 100 ml of benzene was determined with an Ostwald viscosimeter at 20°.

The reaction products were distilled under reduced pressure, and the macromolecular products were suitably purified. Vacuum fractionation of 50 g of the isolated product yielded:

Fraction I, b.p. 68° (8 mm), 7 g
Residue 41 g

Refractionation of Fraction I under normal pressure from a flask having a

Vigreux column yielded a substance having the following constants: b.p. 185-186 (760 mm); n_D^{20} 1.4090; d_4^{20} 0.8255. For acetaldehyde dibutyl acetal, the literature [11] gives: b.p. 184-185° (760 mm); n_D^{20} 1.4090; d_4^{20} 0.8267.

The constants cited therefore indicate that the substance was the dibutyl acetal, which has already been prepared several times. The residue was a light-yellow polymer; before reprecipitation, it had the following constants: n_D^{20} 1.4560; d_4^{20} 0.9287; η 0.684 centipose; M 1439.

This polymer was reprecipitated: A solution of the polymer (30 g) in diethyl ether (120 ml) was filtered, and ethanol (240 ml) was added; no precipitation of polymer occurred. Distilled water (30 ml) was then added cautiously to the solution. The solution rapidly became turbid, and polymer gradually separated. The latter was separated from the solvents, which were then distilled, yielding, as residue, a second polymer fraction. In order to purify them further, the polymer fractions were heated at 90-100° under low pressure (15 mm) for six hours. The characteristics of the resulting fractions are given in Table 2.

TABLE 2

Characteristics of Polymer Fractions Obtained by Reprecipitation

Fraction No.	Molecular weight determined cryoscopically in benzene	n_D^{20}	Viscosity of soln. of 1 g polymer in 100 ml benzene (centipoise)	Yield (%)
1	2112	1.4600	0.701	74
2	682	1.4500	0.653	18

TABLE 3

Variation of the Refractive Index of the Reaction Mixture during the Polymerization of Butyl Vinyl Ether

Temp. of reaction mixture (°C)	n_D^{20}	Note
97	1.4060	Refractive index measurements were made at 20-min. intervals. At the end of the experiment, the resulting polymer had n_D^{20} 1.4560.
97	1.4080	
97	1.4120	
97	1.4220	
97	1.4320	
104	1.4420	
104	1.4480	
104	1.4520	
104	1.4540	
104	1.4560	
97	1.4560	

fractionation macromolecular products remained in the flask. Further fractionations of the fractions yielded two substances. The first had the following constants: b.p. 117-118° (760 mm); n_D^{20} 1.3990; d_4^{20} 0.8106; which identifies it with butyl alcohol, for which the literature gives [13]: b.p. 117.6-117.7°; n_D^{20} 1.3997; d_4^{20} 0.8095.

The second compound had b.p. 185-186° (760 mm); n_D^{20} 1.4087, d_4^{20} 0.8262.

These constants correspond to the dibutyl acetal $\text{CH}_3\text{CH}(\text{OC}_4\text{H}_9)_2$ [12]. All of the results obtained in these experiments are summarized in Table 4.

3. Investigation of the Conditions for the Termination of the Polymerization Processes of Butyl Vinyl Ether by Addition of Butyl Alcohol during the Polymerization. The procedure described in Section 2 was employed. We made preliminary observations on the course of the polymerization process, which was followed by the changes occurring in the refractive index of the reaction mixture. Refractive index measurements were made at 20-minute intervals. The results are given in Table 3.

In the course of these investigations we selected four points at which to make additions of butyl alcohol, namely, when the refractive index of the mixture attained the following values: 1.4120, 1.4220, 1.4320, 1.4420. In every experiment, as soon as the refractive index attained the required value, 74 g of butyl alcohol was added to the reaction mixture. After this the experiment was continued for a further two hours.

The products were vacuum-fractionated, and two main fractions were isolated: the first having b.p. 41-43° (15 mm), and the second b.p. 80-82° (15 mm). After the

TABLE 4

Characteristics of Products Obtained by Termination of the Polymerization Process by Means of Butyl Alcohol

Expt. No.	n_D^{20} of reaction mixture at which butyl alcohol added	Amounts of substances obtained in fractionation (%)			Refractive indices of polymers obtained
		Butyl alcohol	Dibutyl acetal	Polymer	
1	1.4120	26.5	59	11.5	1.4165
2	1.4220	33.2	44.5	17.4	1.4360
3	1.4320	34.6	39.2	20.2	1.4520
4	1.4420	36.5	30.7	30.2	1.4580

4. Study of the Reactions of a Mixture of Two Molecular Proportions of Butyl Vinyl Ether and One of Butyl Alcohol. The mixtures investigated contained 37 g of butyl alcohol to 100 g of butyl vinyl ether. The procedure was as described in Section 2. The experiments yielded light-yellow products of low viscosity. Vacuum fractionation of such a product (50 g) yielded:

Fraction I	b.p. 68-72° (8 mm), 29.5 g
Fraction II	b.p. 75-135° (8 mm), 0.4 g
Fraction III	b.p. 135-138° (8 mm), 5.5 g
Residue	13.8 g

Fraction I, after purification by further fractionation, had the following constants: b.p. 186-187° (760 mm); n_D^{20} 1.4088; d_4^{20} 0.8258. It follows from these constants that it was the dibutyl acetal [12].

Fraction III was again fractionated under reduced pressure, and it yielded a product of b.p. 137-138° (8 mm) and having the following constants: n_D^{20} 1.4259; d_4^{20} 0.8661, found MR 81.04; calculated $C_{16}H_{34}O_3$ MR 81.017.

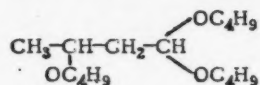
Found: M 266

$C_{15}H_{32}O_3$. Calculated: M 274

Found %: C 69.76, 69.60; H 12.45; 12.38

$C_{16}H_{34}O_3$. Calculated %: C 70.00 H 12.49

From these results we concluded that the substance was 1,1,3-tributoxybutane —



The residue in the flask (not reprecipitated) had the following constants: n_D^{20} 1.4480; d_4^{20} 0.9073; M 564; η 0.646 centipoise. It was a low-molecular-weight polymer of butyl vinyl ether.

5. Synthesis of 1,1,3-Tributoxybutane. To 174 g (1 mole) of acetaldehyde dibutyl acetal, 4 g of a 5% solution of ferric chloride in butyl alcohol was added. The mixture was stirred and heated in a flask in a water bath at 48°. Butyl vinyl ether (50 g, i.e., 0.5 mole) was then added dropwise, the rate of addition being regulated so that the temperature remained in the range 48-50°. After the whole of the ether had been added, the experiment was continued for one hour further. The catalyst was then neutralized with anhydrous sodium carbonate powder (5 g). The mixture was stirred for three hours, and then filtered. The product was 215 g of a colorless liquid. Vacuum fractionation yielded:

Fraction I	b.p. 40-70° (8 mm), 130 g
Fraction II	b.p. 80-140° (8 mm) (major portion at 138°), 62 g
Fraction III	b.p. 145-195° (8 mm), 10 g
Residue	7 g

Fraction I, after purification by refractionation, had the following constants: b.p. 184-185° (754 mm); n_D^{20} 1.4084; d_4^{20} 0.8270. It therefore consisted of the dibutyl acetal [12].

Fraction II, after refractionation, had the following constants: b.p. 137-138° (8 mm); n_D^{20} 1.4255; d_4^{20} 0.8655; found MR 81.02, calculated $C_{16}H_{34}O_3$ MR 81.017.

Found: M 269.9
 $C_{16}H_{24}O_3$. Calculated: M 274

Found %: C 70.09; 70.33; H 12.57, 12.49
 $C_{16}H_{24}O_3$. Calculated %: C 70.00 H 12.49

These constants fully confirm the identity of Fraction II with the 1,1,3-tributoxybutane isolated from the product obtained by the polymerization of butyl vinyl ether in presence of butyl alcohol.

In the present investigation, we have not studied Fraction III and the residue.

SUMMARY

1. From reaction products obtained from mixtures of butyl vinyl ether and butyl alcohol, three substances have been isolated: acetaldehyde dibutyl acetal, 1,1,3-tributoxybutane, and polymer.
2. Two polymer fractions, characterized by molecular weight, viscosity in benzene solution, and refractive index, have been obtained.
3. It has been shown that the degree of polymerization can be regulated by addition of butyl alcohol during the polymerization of butyl vinyl ether.
4. 1,1,3-Tributoxybutane has been prepared by the reaction of acetaldehyde dibutyl acetal with butyl vinyl ether.

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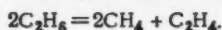
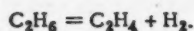
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EFFECT OF PRESSURE ON THE MECHANISM OF THE THERMAL CRACKING OF PARAFFINS

M. G. Gonikberg and V. V. Voevodsky

In this paper we shall attempt to reach some conclusions concerning the mechanism of the cracking of paraffins from an analysis of experimental data on the relation between the rate of cracking and the pressure. Until recently these data have been confined to a short range of pressures (not above 25 atm.). It has been established that at moderate pressures (a few atmospheres), the rate of cracking generally increases with increase in pressure (the decompositions of ethane at 750° and 800° [1], propane at 600° [2], butane at 575° [3] and 600° [2], and heptane at 580° [4]); only in one investigation [5] was a retardation of cracking observed (ethane at 635°). It should be pointed out that the thermal decomposition of butane is intensified by increase of pressure up to a value of 10 atm, but further increase of pressure up to 25 atm has no essential effect on the rate of the process [3].

The cause of the acceleration of the cracking of paraffins by increase in pressure has been attributed by a number of authors to the simultaneous occurrence of decomposition reactions proceeding according to uni-molecular and bimolecular schemes. Thus, for the decomposition of ethane the following reactions have been proposed [3]:



and the acceleration of cracking by increase in pressure has been explained by the acceleration of the bimolecular reaction (the second).

It has been recently established, however, that high pressure (of the order of hundreds and thousands of atmospheres) does not accelerate, but, on the contrary, retards the cracking of paraffins.

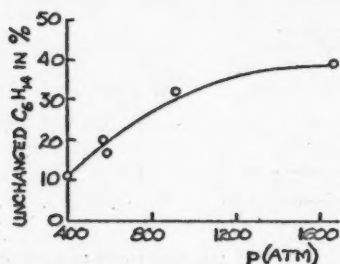


Fig. 1. Effect of pressure on the progress of the thermal cracking of hexane at 430° ($\tau = 3$ hr.)

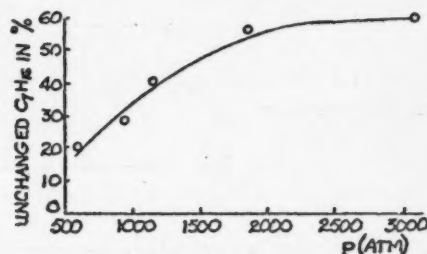


Fig. 2. Effect of pressure on the progress of the thermal cracking of heptane at 420° ($\tau = 3$ hr.)

Figures 1 and 2 show the results of an investigation [6] of the thermal cracking of hexane at 430° and at pressures of 390-1680 atm., and of heptane at 420° and 620-3100 atm; these indicate the great increase in the proportion of unchanged hydrocarbon at the high pressures. It was shown also that the observed retardation of cracking could not be accounted for by the displacement of a chemical equilibrium. Similar conclusions may be drawn also from recent work on the thermal cracking of propane at 600° and at 98 and 197 atm., and of butane at 550° and at pressures of 104 and 172 atm. [7]. It should be noted also that with increase in pressure the yield of low-boiling cracking products is reduced, and there is an increase in the relative content of the higher-boiling (in comparison with the original) hydrocarbons [6].

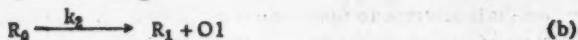
Thus, at moderate pressures (a few atmospheres) cracking is generally accelerated by increase in pressure,

and at high pressures (hundreds and thousands of atmospheres) it is retarded. Let us examine whether a chain mechanism for the decomposition of the paraffin R_0H is consistent with these conditions.

Let us assume, as is usual, that the initiation of chains results from the breakdown of an R_0H molecule into radicals that are shorter in length, and these react with a molecule of the original hydrocarbon with formation of R_0 radicals:



The radical R_0 may either break down with formation of a shorter radical R_1 and an olefin O_1 , or react with an olefin molecule and form a longer radical R_2 :



The resulting radicals may react in their turn with molecules of the original hydrocarbon, and so continue the chain; for example:



[see the right-hand side of the equation (a)].

Finally, chain termination may occur either at the wall (k_5), or by reactions (recombination or disproportionation) of the radicals R_0 and R_1 ($R_0 + R_0 \xrightarrow{k_6} R_0H$; $R_0 + R_1 \xrightarrow{k_7} R_1H$; $R_1 + R_1 \xrightarrow{k_8} R_1H$).

We exclude from consideration all reactions associated with the formation of the longer (in comparison with the original hydrocarbon) radicals R_2 and their further reaction. These reactions appear to play an important part in the cracking of paraffins to which olefins have been added, but they cannot form the main chain-breaking process in absence of additions, particularly at high pressures [8].

Under stationary conditions, when the length of the chain is considerable:

$$k_4(R_0) = k_4(R_1)(R_0H) \quad (1)$$

(the parentheses indicate concentrations). The rate of chain initiation is $2k_1(R_0H)$. We shall now write an expression for the reaction rate w equal to the product of the rate of initiation of chains and the rate of their growth, divided by the rate of chain termination:

$$w = \frac{2k_1(R_0H) \cdot k_4(R_1)(R_0H)}{k_5(R_0) + k_6(R_0)^2 + k_7(R_1)(R_0) + k_8(R_1)^2} \quad (2)$$

Expressing the rate in terms of the concentration of the original hydrocarbon (R_0H), taken as unity, and substituting for R_1 from (1), we obtain:

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_5 + \left[k_6 + \frac{k_2k_7}{k_4} \cdot \frac{1}{(R_0H)} + \frac{k_2^2k_8}{k_4^2} \cdot \frac{1}{(R_0H)^2} \right] (R_0)} \quad (3)$$

Let us examine the possible cases of the preferential termination of chains by one of the reactions enumerated.

a) Chain termination occurs preferentially at the walls, when:

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_5} \quad (4)$$

i.e., the reaction rate (in the units indicated) is independent of the pressure (if we neglect the effect of pressure on the rate constants k_1 , k_2 , and k_5).

b) Chain termination occurs preferentially on radicals of the original hydrocarbons:

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_6(R_0)} \quad (5)$$

From the condition for a stationary state we find:

$$2k_1(R_0H) = k_6(R_0)^2 \quad (6)$$

From (5) and (6) we obtain:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1}{k_6}} k_2 (R_0H)^{-\frac{1}{2}} \quad (7)$$

i.e., the reaction rate falls with increase in (R_0H) : the reaction is retarded by increase in pressure.

c) Chain termination occurs preferentially on the short radicals R_1 :

$$\frac{w}{(R_0H)} = \frac{2k_1k_4^2}{k_2k_8} \cdot \frac{(R_0H)^2}{(R_0)} \quad (8)$$

From the condition for a stationary state we find:

$$2k_1(R_0H) = k_8(R_1)^2 \quad (9)$$

From (1), (8), and (9) we obtain:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1}{k_8}} k_4 \cdot (R_0H)^{\frac{1}{2}} \quad (10)$$

i.e., the reaction rate rises with increase in (R_0H) : the reaction is accelerated by increase in pressure.

d) Chain termination occurs preferentially by the interaction of the radicals R_0 and R_1 :

$$\frac{w}{(R_0H)} = \frac{2k_1k_4}{k_7} \cdot \frac{(R_0H)}{(R_0)} \quad (11)$$

From the condition for a stationary state we find:

$$2k_1(R_0H) = k_7(R_0)(R_1) \quad (12)$$

From (1), (11), and (12) we obtain:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1k_2k_4}{k_7}} \quad (13)$$

i.e., the reaction rate is independent of pressure.

The data cited above concerning the effect of pressure on the rate of cracking and the analysis of various cases of the preferential termination of chains in the thermal cracking of paraffins give reason to suppose that at moderate pressures chain termination occurs preferentially by reaction with "short" radicals (R_1), and at high pressures by reaction with "long" radicals (R_0). This supposition, however, should be provided with some basis by an examination of the relative probabilities of these two types of termination and the change in the relative probability with increase in pressure.

The probabilities of chain termination on R_0 and on R_1 (δ_{R_0} and δ_{R_1}) are given by the expressions:

$$\delta_{R_0} = \frac{k_6(R_0)^2}{k_2(R_0)} = \frac{k_6}{k_2} (R_0) \quad (14)$$

and

$$\delta_{R_1} = \frac{k_8(R_1)^2}{k_7(R_1)(R_0H)} = \frac{k_8(R_1)}{k_7(R_0H)} \quad (15)$$

It follows from (1) that:

$$\frac{(R_0)}{(R_1)} = \frac{k_4}{k_2} (R_0H),$$

so that

$$\frac{\delta_{R_0}}{\delta_{R_1}} = \frac{k_4^2 k_6}{k_2^2 k_8} (R_0H)^2 \quad (16)$$

The ratio of the probabilities of termination on R_0 and on R_1 is therefore proportional to the square of the concentration of the original hydrocarbon. In other words, this ratio increases very rapidly with rise in pressure, which is a qualitative confirmation of the supposition made above.

An approximate quantitative examination of this question also leads to the conclusion that an increase in pressure of, say, from 5 to 500 atm. may result in the change indicated in the process of chain termination. Let

us find the orders of magnitude of the rate constants entering into the expression (16):

$$\frac{\delta R_0}{\delta R_1} \approx \frac{f_4^2 f_6}{f_2^2 f_8} \left(10^{-23} e^{\frac{E_2 - E_4}{RT}} \cdot \frac{10^{19}}{T} \cdot 760 \cdot P_{R_0H} \right)^2.$$

(f_2 , f_4 , f_6 , and f_8 are the steric factors of the corresponding reactions; T is the absolute temperature; P_{R_0H} is the pressure of the hydrocarbon (atm).

The activation energies E_2 and E_4 can be approximately evaluated from the energy of rupture of a C-C bond into free radicals [9, 10]:

$$E_2 \approx 12-20 \text{ kcal/mole}$$

and from data concerning the kinetics of the reactions



$$E_4 \approx 7-8 \text{ kcal/mole.}$$

Values of $\delta R_0/\delta R_1$

p(atm)	$E_2 - E_4$ (kcal/mole)	
	5,000	12,000
5	$3.7 \cdot 10^{-4} F$	8.3 F
500	3.7 F	$8.3 \cdot 10^4 F$

Substituting $T = 700^\circ K$ we find the values of $\delta R_0/\delta R_1$ given in the table (for extreme values of the difference $E_2 - E_4$).

The value of $F = \frac{f_4^2 f_6}{f_2^2 f_8}$ can be roughly evaluated from the following data:

$$\frac{f_6}{f_8} \approx 10^{-2} - 10^{-3},$$

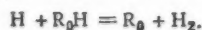
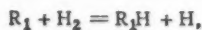
since the recombination of "long" radicals is considerably hindered sterically.* The value of f_4 may be taken to be about 10^{-3} , by analogy to $CH_3 + RH$ reactions [13]. The values of f_2 for the rupture of C-C bonds in free radicals are very low, being about $10^{-4} - 10^{-5}$ [10]. Hence, accurate within a factor of ten, we may write:

$$F \approx 10^{-2} \left(\frac{10^{-3}}{10^{-4}} \right)^2 \approx 1.$$

It will be seen from this approximate calculation that, for a very extensive range of values of the difference $E_2 - E_4$, the ratio $\delta R_0/\delta R_1$ may change from values $\ll 1$ to values $\gg 1$ as we pass from 5 to 500 atm. The variation of the kinetics of the thermal cracking of paraffins with rise in pressure may therefore be explained by a change in the nature of the predominant chain-terminating reaction.

In the above analysis we have excluded from consideration the reaction (c), which leads to the formation of radicals of higher molecular weight than that of the original hydrocarbon (i.e., the alkylation reaction), and also the subsequent reactions of these radicals. It is natural to suppose that the alkylation of paraffins by olefins, with formation of substances higher in molecular weight than the original substances, will be considerably accelerated by increase in pressure. In the case we have considered these reactions therefore have a modifying effect on the retardation produced by high pressure on thermal cracking. In the absence of alkylation reactions, this retarding effect of pressure would be much more strongly marked.

Actually, the results of one of the investigations cited [6] show that under a hydrogen pressure of about 200 atm, the alkylation and polymerization reactions occurring in the cracking of hexane and heptane are suppressed owing to the hydrogenation of the olefins [14], and this results in a considerable reduction in the rate of cracking, as measured by the proportion of unchanged original hydrocarbon. However, further increase in the hydrogen pressure to 1200 atm, [6] results in the acceleration of thermal decomposition. This is probably due to participation of hydrogen in chain propagation, according to the scheme:



A similar acceleration of the thermal decomposition of a hydrocarbon due to increase in the partial pressure of hydrogen (from 200 to 400 mm Hg) was observed recently in the case of propane [15].

* Thus, for the recombination of isopropyl radicals it is considered that f is about 5×10^{-2} [12], whereas for the recombination of methyl radicals at moderate temperatures f is about unity [13].

In conclusion, let us supplement our analysis by a consideration of the effect of pressure on the values of the rate constants for the reactions examined. It is known that at pressures of up to 2000 - 3000 atm, rate constants of decomposition reactions are slightly reduced. Over the same range of pressures the rate constants of addition and exchange reactions may increase considerably, as is observed, in particular, for esterification, hydrolysis, polymerization, and many other reactions. With rise of pressure, therefore, k_1 and k_2 diminish somewhat, and k_4 , k_5 , k_6 , k_7 , and k_8 increase. When there is preferential chain termination at the walls, consideration of the effect of pressure on the rate constants leads to the conclusion that there will be a certain retardation of cracking by increase of pressure, in accordance with equation (4). As regards equations (7) and (10), which appear to characterize the two main types of chain termination during cracking, consideration of them shows that the taking of the effect of pressure on these rate constants into account cannot influence the sign of the pressure effect in these two cases. Thus, the inferences that we have made above concerning the change in the nature of the chain-termination process as the pressure rises still hold good.

SUMMARY

1. An analysis of experimental data on the effect of pressure on the rate of thermal cracking of paraffins leads to the conclusion that rise in pressure in the range 1 - 10 atm, approximately, generally accelerates cracking, whereas in the range 100 - 1000 atm, approximately, it retards it.

2. A scheme, consistent with the observed effects of pressure on the rate of the process, has been given for the mechanism of the thermal cracking of paraffins.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 61. REACTIONS OF POLYESTER MACROMOLECULES

V. V. Korshak and S. V. Vinogradova

Our investigation [1] of the polycondensation of 1,6-hexanediol with sebacic acid showed that only at the beginning of the process does reaction between the original substances occur with formation of low-molecular-weight polyesters (molecular weight up to 900, i.e., up to the trimer). The further polycondensation process, as a result of which the macromolecular polyester is formed, proceeds by interaction of the already formed polyester molecules, which are at first of low molecular weight, and later of high molecular weight. Toward the end of the reaction the interaction between the polyester macromolecules themselves becomes the main feature of the process, and determines the final result.

On the basis of these results it was concluded that the molecules of macromolecular compounds are of fairly high reactivity and can react with one another through their end groups at an appreciable rate. This conclusion refutes the previously widely held idea that macromolecules have negligible reactivity owing to their low mobility and to the high viscosity of the surrounding medium. It will be evident that, in all transformations of macromolecular compounds, it will be necessary to take into account the reactions of the macromolecules among themselves as forming an essential factor in the process. However, since our inferences were made on the basis of an investigation of the kinetics of the process, i.e., indirectly, it is necessary to find more direct and reliable proofs of the correctness of these ideas. With this object in view we have carried out the present investigation, in which we have studied the reaction between polyester macromolecules having different end groups.

The polyesters studied consisted of those synthesized by us from sebacic acid and 1,6-hexanediol and obtained (1) with excess of acid and therefore having carboxyl end groups, and (2) with excess of diol and therefore having hydroxyl end groups. A third polyester was prepared from diethyl sebacate and ethylene glycol, and had ethoxyl end groups. The detailed characteristics of these polyesters are given in Table 1.

TABLE 1
Properties of the Original Polyesters

No.	Starting substances	Molar ratio	Properties of the polyester		
			Spec. viscosity	Mol. wt.	End groups
1	Sebacic acid + 1,6-hexanediol	1.3: 1	0.037	1265	Carboxyls
2	Sebacic acid + 1,6-hexanediol	1: 1.3	0.045	1533	Hydroxyls
3	Diethyl sebacate + ethylene glycol	1.3: 1	0.038	1327	Ethoxyls

The polyesters were purified by reprecipitation from benzene solution by means of petroleum ether. Three mixtures for reaction were then prepared from them: 1 + 3, 1 + 2, and 2 + 3,

taken in equal amounts by weight. The mixtures were heated for ten hours at 200° under reduced pressure (2 mm Hg). Samples for test were taken at definite intervals of time. The results are given in Table 2.

TABLE 2
Polycondensation of Polyesters

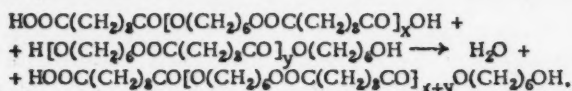
No.	Duration of heating (hr)	Change in the spec. viscosity of the polyester mixture (0.5%)		
		1 + 2	1 + 3	2 + 3
1	0	0.04	0.04	0.04
2	1	0.07	0.04	0.06
3	2	0.08	0.04	0.08
4	4	0.11	0.04	0.11
5	7	0.13	0.04	0.13
6	10	0.14	0.04	0.13

As will be seen from Table 2, the three polyester mixtures behaved very differently: whereas the 1 + 2 and the 2 + 3 mixtures showed a high increase in the viscosity of their solutions after being heated, the 1 + 3 mixture was completely unaffected. For greater clarity we have represented the viscosity changes graphically (Fig. 1).

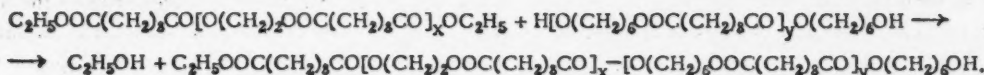
Fig. 1 shows that, when the polyester mixtures 1 + 2, and 2 + 3 are heated, there is a smooth rise in viscosity, i.e., a continuous increase in the molecular weight of the product of the reaction of the two polyesters, whereas the 1 + 3 mixture undergoes no change in viscosity, and therefore in molecular weight. This indicates quite definitely

the presence of interaction between the original polyesters in the case of the first two mixtures and the absence of any reaction in the case of the third mixture. We may, therefore, consider that we have fully proved the occurrence of reaction between two polyesters resulting in the growth of the macromolecule and the formation of a polyester of higher molecular weight.

The difference in the behaviors of the polyester mixtures that we prepared is readily understood when we consider the differences in the nature of the end groups of the polyesters and the effects that they have on the reactivities of the molecules. Polyester No. 1 was prepared with an excess of sebacic acid and all of its end groups are therefore carboxyls. Polyester No. 2 was prepared with an excess of 1,6-hexanediol, and has hydroxyl end groups. A mixture, therefore, of these two polyesters readily reacts by direct esterification between the carboxyl and hydroxyl groups:

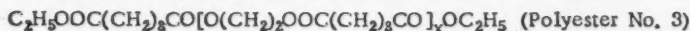
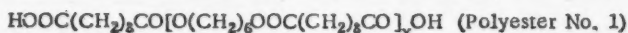


Polyester No. 3 was prepared from diethyl sebacate and has ethoxyl end groups; it therefore reacts readily with Polyester No. 2, which has hydroxyl end groups. In this case transesterification occurs by alcoholysis, and ethanol is formed in accordance with the equation:



As we have shown previously for the polycondensation of bis(2-hydroxyethyl) sebacate [2], the alcoholysis reaction can be used successfully for the synthesis of polyesters. In the present case we have an example of such a reaction in which the alcoholysis occurs not between molecules of the original monomers, but between polyester macromolecules. The smooth course of the alcoholysis reaction in this case proves that there is no difference in principle between the macromolecules and the original monomers with respect to the possibility of the occurrence of a given reaction.

In the case of the mixture of Polymers No. 1 and 3, the picture undergoes a radical change. The end groups of these polyesters are carboxyls and ethoxyls. Interaction between these, either by direct esterification or by alcoholysis, is impossible, as can be readily seen by an examination of the formulas of these polyesters:



The only possible method of interaction is by acidolysis with separation of sebacic acid or its diethyl ether; but, as we have shown in a previous paper [3], the acidolysis reaction proceeds much less readily than the reactions of alcoholysis and direct esterification. In the present case the occurrence of polycondensation by acidolysis is rendered even less likely by the fact that sebacic acid is considerably less volatile than adipic acid, the esters of which were the subject of our previous investigation. This provides the explanation of the fact that the polyester mixture 1 + 3 does not change when heated, its viscosity in solution and molecular weight, unlike those of the first two mixtures, undergoing no change.

In general, therefore, our results confirm the rule that we have previously noted: in polycondensation the reaction rate and degree of conversion are determined not by the nature of the low-molecular-weight products formed, but by their volatility [3]. If, in fact, we examine the volatilities of the low-molecular weight polycondensation products in the case of our three polyester mixtures, then it will be immediately obvious that there is a correlation between the degree of conversion (in other words, the molecular weight of the polymer) and the volatility of the low-molecular-weight reaction product. In the case of the polyester mixture 1 + 2, the low-molecular-weight reaction product is water, and for the mixture 2 + 3 the corresponding product is ethanol; i.e., both substances are very volatile. Correspondingly, the molecular weight of the polyester rises from 1400 in the original mixture to 4500. In the case of the polyester mixture 1 + 3 the only possible low-molecular-weight products are

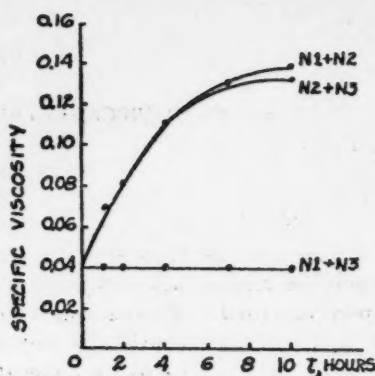


Fig. 1

sebacic acid and its ester. Both of these substances are of high boiling point and low volatility, and, as a result, there is naturally no rise in molecular weight in this case.

In conclusion we must point out that this investigation of polyesters having carboxyl, hydroxyl, and ethoxyl end groups has confirmed our previous results on the polyesterification reaction and has shown that polyester macromolecules readily react with one another forming compounds of higher molecular weight. A decisive part in this is played by a factor determined by the volatility of the low-molecular-weight product that separates in the given reaction. If a readily volatile product separates, reaction will proceed owing to the rapid displacement of the equilibrium toward the right, but when the low-molecular-weight reaction product is of low volatility, the equilibrium will not be displaced toward the right and no polyesterification will occur.

SUMMARY

1. A study has been made of reactions in three mixtures, each containing two polyesters having different end groups. Three polyester components, having carboxyl, hydroxyl, and ethoxyl end groups respectively, are used.
2. It has been found that the polyester having hydroxyl end groups reacts with the polyesters having carboxyl and ethoxyl end groups.
3. It has been found that the polyester having carboxyl end groups does not react with the polyester having ethoxyl end groups.
4. It has been shown that a decisive factor for the occurrence of polycondensation is the volatility of the low-molecular-weight product that separates; high volatility leads to a displacement of the equilibrium to the right and so to the growth of the polymer molecules.
5. It has been shown that macromolecules have fairly high reactivities, so that they are capable of undergoing the same reactions as the monomers are.

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* See Consultants Bureau Translation, page 483.

** " " " " " 847.

BRIEF COMMUNICATIONS

PREPARATION OF TETRAPHENYL- AND TETRA-*p*-TOLYLY-LEAD BY THE DECOMPOSITION OF ARENEDIAZONIUM FLUOBORATES WITH LEAD - SODIUM ALLOY

A. N. Nesmeyanov and L. G. Makarova

By the decomposition of benzenediazonium fluoborate with lead powder in acetone, one of us, together with Kocheshkov and Nad [1], has prepared tetraphenyllead in 15% yield. It was not found possible to obtain any organolead compound when other arenediazonium fluoborates were decomposed with lead powder. It is now found, however, that if, instead of lead powder, a lead-sodium alloy (containing 10% sodium) is used for the decomposition of arenediazonium fluoborates in acetone, tetraphenyllead is obtained in 30% yield, and tetra-*p*-tolyllead is obtained in 15% yield.

EXPERIMENTAL

Preparation of Tetraphenyllead. Over a period of 90 minutes 7.5 g of a lead-sodium alloy (10% Na) was introduced into a cooled (ice water) vigorously stirred (Witt stirrer) suspension of 10 g of benzenediazonium fluoborate in 60 ml of dry acetone. Nitrogen was evolved. The initial temperature was +4°, and the maximum temperature was +13°. When the whole of the alloy had been added, the mixture, cooled with ice water, was stirred for four hours. On the next day the acetone was distilled off, and the residue was washed with ether and then treated in an extractor with chloroform. The chloroform was evaporated off, and the residue was washed with ether and crystallized from chloroform. The melting point, and also a mixture melting point with known tetraphenyllead, was 225°. The yield was 2.07 g (30%). The residue in the extraction thimble did not burn when heated with copper oxide.

Preparation of Tetra-*p*-tolyllead. Over a period of ten minutes 7.2 g of a lead-sodium alloy (10% Na) was introduced into a cooled (by ice water to +6°) stirred suspension of 10.3 g *p*-toluenediazonium fluoborate in 60 ml of dry acetone. After 1½ minutes evolution of nitrogen began and the temperature rose to +14°. When the addition of alloy was complete, the mixture, cooled with ice water, was stirred for one hour, and was then set aside overnight at room temperature. On the next day the precipitate was filtered off by suction, washed with ether, and treated in an extractor with chloroform. The residue remaining after evaporation of the chloroform was washed with ether and crystallized from a mixture of acetone and chloroform. The yield was 1.11 g (15.6%). After recrystallization from chloroform, it melted at 240° (for the melting point of tetra-*p*-tolyllead the literature [2] gives 240°). When acetone was evaporated from the filtrate from the original precipitate, there remained a black, viscous mass, which did not contain lead. The residue in the extraction thimble did not contain any organolead compounds (tested with copper oxide).

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N. D. Zelinsky Institute of Organic Chemistry
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DIAMAGNETIC SUSCEPTIBILITY OF SOME ORGANIC COMPOUNDS

M. A. Luferova and Ya. K. Syrkin

By a method that has been described previously [1] we have measured the diamagnetic susceptibilities of twenty organic compounds, namely, certain 1- and 2-substituted naphthalenes, some o-, m-, and p-disubstituted benzenes, and some urea derivatives. The values found for the molecular susceptibilities are given in the table.

TABLE

Substance	$-\chi \cdot 10^6$	Substance	$-\chi \cdot 10^6$
1-Naphthol	95.22	o-Nitrophenol	68.97
2-Naphthol	98.25	m-Nitrophenol	65.91
1-Naphthylamine	91.85	p-Dichlorobenzene	81.73
2-Naphthylamine	98.00	1-Chloro-4-iodobenzene	99.42
1-Methylnaphthalene	102.15	p-Iodotoluene	101.31
2-Methylnaphthalene	108.83	Carbanilide	134.05
1-Nitronaphthalene	98.47	$C_6H_5NH \cdot CO \cdot NH \cdot C_6H_5$	
2-Naphthalenesulfonyl chloride	121.91	3-Nitrocarbanilide	148.1
2-Naphthalenesulfonamide	127.60	$C_6H_5NHCONHC_6H_4(NO_2)$	
o-Nitroaniline	67.64	2-Methylcarbanilide	154.0
m-Nitroaniline	59.77	$C_6H_5NHCONH \cdot C_6H_4(CH_3)$	
p-Nitroaniline	63.36		

In all of the investigated cases the diamagnetic susceptibilities (DS) of 2-substituted naphthalenes are greater, than those of the corresponding 1-substituted naphthalenes in absolute magnitude. As is well known, a similar regularity is to be observed also for the dipole moments of 1- and 2-substituted naphthalenes. Pascal's additive values are different from those found experimentally. Thus, for naphthol the additive value of the DS is 96.14, for naphthylamine it is 99.07, for methylnaphthalene it is 103.4, and for nitronaphthalene it is 96.71.

The benzene derivatives were studied in relation to the indications given in the literature that the maximum DS is possessed by ortho derivatives when the groups are ortho-para-orienting, and by the meta derivatives when the groups are meta-orienting [2]. In the case of the nitroanilines, the order of the DS values is as follows:

ortho > para > meta,

For 1-chloro-4-iodobenzene and the last two compounds in the table, the respective additive DS values are 107.27, 135.21 and 141.90. It will be seen that these values differ appreciably from the experimental values. A detailed consideration of the results given in the table, and also of data for other compounds, will form the subject of a further paper.

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DIPOLE MOMENTS OF SOME ORGANIC MOLECULES

E. A. Shott-Lvova and Ya. K. Syrkin

By means of the heterodyne method in benzene solution at 25° we have measured the dipole moments of a number of organic compounds, including hydroxy compounds, azonaphthalenes and their derivatives, and also derivatives of adipic acid. Below we give a table in which we indicate the range of concentrations studied (mole fractions), the total polarizations P , the electron polarizations P_E , and the values of the dipole moments. The dipole moment of 4-cyclohexyloxy pyridine differs greatly from the value calculated by vector addition, which indicates the appreciable part played by the oxonium state of the oxygen in this compound. In the case of 4-phenoxypyridine, the effect of the phenyl group is felt: this may displace an electron toward itself and give a component moment at an angle of 110°, which must lead to a diminution in the moment, as compared with the first compound in the table. Unlike these compounds, vinyl ethers have moments close to the value of the moment of the linkage C-O-C in the usual ethers.

A comparison of 1- and 2-substituted naphthalenes shows that the moment of 2,2'-azonaphthalene is greater than that of 1,1'-azonaphthalene. A similar regularity is observed also for a number of other α - and β -derivatives. The dipole moments of the adipic acid derivatives were determined in connection with the question of internal rotation about single bonds. The moments of adiponitrile and diethyl adipate were determined also at 50°; a slight dependence on temperature was observed. A detailed discussion of the results will appear in the future.

TABLE

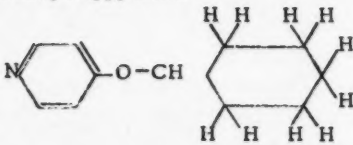
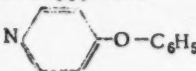
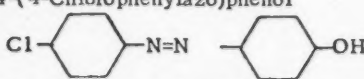
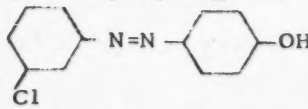
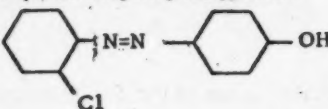
No.	Compound	Concentration (mole fraction)	P	P_E	$\mu \cdot 10^{18}$
1	4-Cyclohexyloxy pyridine 	0.074 - 0.013	300.9	51.32	3.46
2	4-Phenoxypyridine 	0.01 - 0.012	181.2	47.03	2.54
3	Phenyl vinyl ether $\text{CH}_2=\text{CH}-\text{O}-\text{C}_6\text{H}_5$	0.017 - 0.098	62.88	37.53	1.1
4	Octyl vinyl ether $\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2)_7\text{CH}_3$	0.017 - 0.044	79.53	49.53	1.2
5	Butyl 1-chloroethyl ether $\text{C}_4\text{H}_9\text{OCH}(\text{Cl})\text{CH}_3$	0.019 - 0.056	125.96	36.42	2.07
6	1,1'-Azonaphthalene	0.012 - 0.022	98.27	91.12	0.59
7	2,2'-Azonaphthalene	0.002 - 0.0025	114.96	91.12	1.07
8	4-(4-Chlorophenylazo)phenol 	0.0038 - 0.0046	211.56	55.13	2.74
9	4-(3-Chlorophenylazo)phenol 	0.004 - 0.0045	189.2	55.13	2.54

TABLE -- (continued)

No.	Compound	Concentration (mole fraction)	P	P _E	$\mu \cdot 10^{18}$
10	4-(2-Chlorophenylazo)phenol 	0.0021-0.0035	153.98	55.13	2.18
11	Adiponitrile $\text{CN}(\text{CH}_2)_4\text{CN}$	0.0079-0.015	330.93	29.99	3.81
12	Diethyl adipate $\text{C}_2\text{H}_5\text{OOC}(\text{CH}_2)_4\text{COOC}_2\text{H}_5$	0.009 -0.028	173.18	51.69	2.42
13	Putrescine • $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	0.001 -0.005	148.49	35.31	2.33

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* The literal translation of the Russian is "the diamine of adipic acid". Possibly, adipamide $\text{NH}_2\text{CO}(\text{CH}_2)_4\text{CONH}_2$ is intended. PUBLISHER.

March-April, 1954

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